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BOILING POINTS OF *n*-HEPTANE AND 2,2,4-TRIMETHYLPENTANE OVER THE RANGE 100- TO 1,500-MILLIMETER PRESSURE

By Edgar Reynolds Smith

ABSTRACT

By a comparative dynamic method, using water as the reference standard and ebulliometers of the Świętosławski type, data were obtained from which were developed the following equations to express the relationship between temperature and vapor pressure from 100 to 1,500 mm:
For *n*-heptane,

$$\log_{10} p = 6.905\,113 - \frac{1269.821}{217.110+t}.$$

For 2,2,4-trimethylpentane,

$$\log_{10} p = 6.820\,137 - \frac{1262.707}{221.307+t}.$$

In these equations, p is the vapor pressure in standard millimeters of mercury exerted by the substance at the temperature t in degrees centigrade.

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I. INTRODUCTION

In the comparative dynamic method of measuring the boiling points of liquids, successive measurements are made of the boiling point of the substance under investigation and the boiling point of water, in ebulliometers connected to the same manostat by means of which the pressure can be varied. Thus the data are obtained in the form of a series of corresponding boiling points of the substance and of water under the same pressure [9].[1]

For pressures not far from 1 atmosphere, in particular over the range of 660 to 860 mm, the temperature-pressure relationships of water and

[1] Figures in brackets indicate the literature references at the end of this paper.

of other liquids [1, 4, 6, 10] can be expressed precisely by equations of the type

$$t-t_n=a(p-760)+b(p-760)^2+c(p-760)^3$$

and

$$p-760=q(t-t_n)+r(t-t_n)^2+s(t-t_n)^3,$$

in which a, b, c, q, r, and s, are constants, t is the temperature in degrees centigrade at which the vapor pressure is p, and t_n is the normal boiling point. Over the range of pressures reported in this paper, an exponential type of equation represents the data better than a three-power series, and the following procedure for the computations was found convenient.

From the observations of t_s, the boiling point of the substance under consideration, and t_w, the corresponding boiling point of water, the derivatives, dt_s/dt_w and d^2t_s/dt_w^2, were expressed in the approximate form of finite increments. The former was found to be linear with respect to t_w, and the values of the latter were scattered about an average value and showed no trend, thus indicating that the second derivative was constant. Accordingly, an equation of the type

$$t_s=a+bt_w+ct_w^2 \tag{1}$$

has the proper form to represent the relationship between the corresponding temperatures,[2] and the constants a, b, and c were evaluated next by the method of least squares. Using the equation thus obtained, values of t_s which correspond to a series of reference values of t_w in the measured range were computed. The reference values of t_w and the corresponding pressures taken as primary reference standards were chosen from the recent critical compilation by Osborne, Stimson, and Ginnings [5] and are given in table 1. The computed values of t_s were then tabulated with these corresponding pressures, and the constants A, b, and c in the equation

$$\log p=A-\frac{b}{c+t} \tag{2}$$

were evaluated to fit the tabulated data and thus to obtain a relationship between temperature and pressure. The symbol "log" is used in this paper to denote the logarithm to the base 10. Equation 2 written in the form $t=b/(A-\log p)-c$ is explicit in temperature. Also,

$$\frac{dp}{dt}=\frac{p(A-\log p)^2}{b\log e}; \tag{3}$$

and by integration of eq 3,

$$t_n-t=\frac{b(\log 760-\log p)}{(A-\log 760)(A-\log p)}, \tag{4}$$

in which t_n is the normal boiling point and t is the boiling point at the pressure p. Equation 4 is useful for calculating the normal boiling point from a boiling point measured at any pressure within the range for which eq 2 is applicable.

[2] This equation has been found by A. Zmaczynski to express satisfactorily the same relationship for several substances [9, 11].

TABLE 1.—*Reference values of the vapor pressure of water adopted for comparative ebulliometric measurements over the range of 100- to 2,000-mm pressure*

Temperature	Pressure	Temperature	Pressure
°C	mm	°C	mm
50	92.52	95	633.99
55	118.06	100	760.00
60	149.40	105	906.06
65	187.57	110	1074.58
70	233.72	115	1268.03
75	289.13	120	1489.14
80	355.22	125	1740.77
85	433.56	130	2026.02
90	525.86		

II. APPARATUS AND MATERIALS

Two simple barometric ebulliometers of the type developed by Świętosławski [9] were sealed to a manostat through drying tubes. These tubes contained phosphoric anhydride next to the ebulliometer containing the substance under investigation and calcium chloride next to the ebulliometer containing water. In addition to a tube for filling, a small condenser for distilling out a portion of the charge was sealed to the ebulliometer used to contain the liquid to be measured. The manostat was a vessel of Pyrex glass with a volume of 25 liters and was placed in an insulated casing. The arrangement is shown diagrammatically in figure 1. All joints were of fused Pyrex glass tested for vacuum tightness. Pressures above atmospheric were obtained by the addition of nitrogen to the previously evacuated and nitrogen-filled manostat. After filling the ebulliometer with the liquid under investigation, the filling tube was sealed off, ice water was circulated through the condensers by means of a miniature centrifugal pump, and the boiling point was measured. A portion was then distilled out through the small external condenser, and the boiling point was measured again. No significant difference was detected in any case. The external condenser was then sealed off, and the comparative measurements of temperature were made with a platinum resistance thermometer (coiled-filament type) and a Mueller ther-

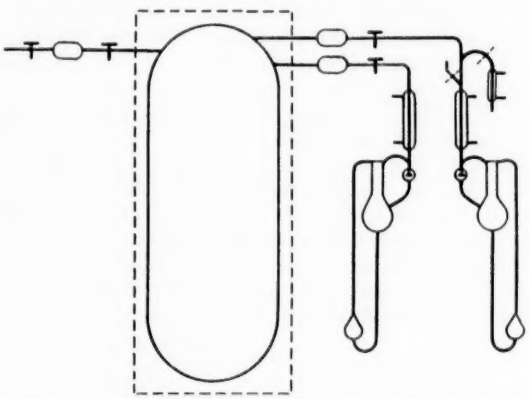

FIGURE 1.—*Arrangement of ebulliometers and manostat.*

mometer bridge, by the method described in other papers from this laboratory [6, 7]. It was unnecessary to thermostat the bridge, since the temperature corrections to the resistances were practically identical for the reference and the measured substance in these comparative measurements.

The temperatures were measured to 0.001° with an average reproducibility of 0.002° to 0.003° and an accuracy estimated at about 0.005° with respect to their values on the international temperature scale. Corrections for the difference in density of water vapor and hydrocarbon vapor in the column above the thermometer coil were estimated to be within the experimental error.

The *n*-heptane and 2,2,4-trimethylpentane were supplied by D. B. Brooks, of the Automotive Power Plants Section of this Bureau. Their preparation, purity, and physical properties have been described in a recent paper by Brooks, Howard, and Crafton, Jr. [2]. When tested in a differential ebulliometer [9], the difference between boiling point and condensation temperature of each substance was only 0.002°.

III. EXPERIMENTAL RESULTS

n-Heptane.—The comparative boiling points of *n*-heptane and water are given in table 2. The expression obtained for the boiling point of *n*-heptane as a function of the corresponding boiling point of water is

$$t=-13.6536+1.025\,711\,t_w+0.000\,950\,92\,t_w^2 \quad (5)$$

The average deviation of the 18 measurements from eq 5 is 0.003°; and there is one exceptional deviation of 0.015° at the sixth point, for which the calculated value is 62.754° as compared with the observed value of 62.739°. If this point is omitted, the average deviation is 0.002° and the greatest deviation is 0.005°. The normal boiling point calculated from eq 5 ($t_w=100°$) is 98.427°. The difference between this and the value of 98.413° reported in an earlier paper [6] is attributed to the more efficient purification of the material used in this work. The temperatures calculated from eq 5 for the standard reference pressures of table 1 are given in table 4, together with those for 2,2,4-trimethylpentane. The equation found to represent the pressure-temperature relationship is

$$\log p=6.905\,113-\frac{1269.821}{217.110+t}. \quad (6)$$

This equation represents the data given in table 4 with an average deviation of 0.04 mm and one exceptionally large deviation of 0.14 mm at the highest pressure. The normal boiling point ($p=760$ mm) calculated from eq 5 is 98.428°. Smyth and Engel [8] have measured the vapor pressure of *n*-heptane between 22.7° (41.4 mm) and 98.4° (760 mm). Considering that their measurements of temperature and pressure were made only to the nearest 0.1° and 0.1 mm, respectively, the agreement of their values with those calculated by eq 6 is within their experimental error and indicates that eq 6 can be used with confidence for extrapolation to pressures at least as low as 40 mm. The relationship

$$t_n=t+315.538\frac{(2.880\,814-\log p)}{(6.905\,113-\log p)}$$

from eq 4 is useful for calculating the normal boiling point from the boiling point at any pressure in the range of 100 to 1,500 mm.

TABLE 2.—*Corresponding boiling points of n-heptane and water*

Boiling point		Boiling point	
n-Heptane	Water	*n*-Heptane	Water
°C	°C	°C	°C
37.076	47.379	83.881	87.923
41.785	51.578	89.084	92.268
46.920	56.135	94.104	96.435
51.938	60.545	99.110	100.562
57.224	65.164	103.990	104.561
62.739	69.955	109.745	109.240
67.984	74.450	114.967	113.460
73.474	79.135	118.285	116.128
78.738	83.594	124.594	121.173

2,2,4-Trimethylpentane (*isooctane*).—The corresponding boiling points of water and 2,2,4-trimethylpentane are given in table 3. The expression found for the boiling point of 2,2,4-trimethylpentane in terms of the corresponding boiling point of water is

$$t = -16.0924 + 1.044\,559 t_w + 0.001\,086\,89 t_w^2. \quad (7)$$

The average deviation of the 16 measurements from eq 7 is 0.002° and the greatest deviation is 0.004°. The normal boiling point calculated from eq 7 is 99.232° as compared with 99.234 reported previously [6] from measurements over the range 660 to 860 mm. The temperatures calculated from eq 7 to correspond with the standard reference pressures are given in table 4, together with those for *n*-heptane. The equation found to represent these pressure-temperature data is

$$\log p = 6.820\,137 - \frac{1262.707}{221.307 + t} \quad (8)$$

with an average deviation of 0.05 mm and one exceptional deviation of 0.16 mm at the highest pressure. No other data on 2,2,4-trimethylpentane could be found for comparison [3]. For calculating the normal boiling point from the boiling point at any pressure in the range of 100 to 1,500 mm, the equation

$$t_n = t + 320.539 \frac{(2.880\,814 - \log p)}{(6.820\,137 - \log p)} \quad (9)$$

may be used.

TABLE 3.—*Corresponding boiling points of 2,2,4-trimethylpentane and water*

Boiling point		Boiling point	
2,2,4-Trimethylpentane	Water	2,2,4-Trimethylpentane	Water
°C	°C	°C	°C
45.329	55.585	92.187	94.392
51.012	60.441	98.441	99.371
57.515	65.945	99.310	100.061
63.484	70.944	104.415	104.091
68.759	75.327	107.670	106.647
74.588	80.133	113.891	111.501
80.254	84.763	119.413	115.777
86.224	89.598	126.439	121.176

TABLE 4.—*Boiling points of n-heptane and 2,2,4-trimethylpentane at standard reference pressures*

Boiling point		Pressure	Boiling point		Pressure
n-Heptane	2,2,4-Trimethylpentane		*n*-Heptane	2,2,4-Trimethylpentane	
°C	°C	mm	°C	°C	mm
40.009	38.853	92.52	98.427	99.232	760.00
45.637	44.646	118.06	104.530	105.569	906.06
51.312	50.494	149.40	110.681	111.961	1074.58
57.035	56.396	187.57	116.879	118.406	1268.03
62.806	62.353	233.72	123.125	124.906	1489.14
68.624	68.363	289.13	129.418	131.460	1740.77
74.489	74.428	355.22			
80.402	80.548	433.56			
86.363	86.722	525.86			
92.371	92.950	633.99			

Values of the temperature and rates of change of pressure with temperature at even values of the pressure are given in table 5 for both *n*-heptane and 2,2,4-trimethylpentane.

An expression for the logarithm of the relative volatility, defined as the ratio of the vapor pressures of the two pure substances, may be obtained by subtracting eq 8 from eq 6.

TABLE 5.—*Values of pressure, temperature, and rates of change of pressure with temperature for n-heptane and 2,2,4-trimethylpentane*

Pressure	*n*-Heptane		2,2,4-Trimethylpentane	
	Temperature	*dp/dt*	Temperature	*dp/dt*
mm	°C	mm/°C	°C	mm/°C
50	[a] 26.80	[a] 2.46	[a] 25.26	[a] 2.39
100	41.767	4.363	40.658	4.237
200	58.693	7.688	58.109	7.448
300	69.661	10.666	69.438	10.319
400	77.988	13.430	78.049	12.978
500	84.787	16.040	85.089	15.485
600	90.579	18.530	91.091	17.875
700	95.653	20.923	96.352	20.169
760	98.428	22.319	99.232	21.507
800	100.185	23.234	101.055	22.383
900	104.293	25.474	105.321	24.528
1000	108.059	27.653	109.233	26.612
1200	114.789	31.851	116.229	30.624
1400	120.700	35.871	122.380	34.461
1600	125.993	39.740	127.892	38.150
1800	[a] 130.80	[a] 43.48	[a] 132.90	[a] 41.71

[a] Extrapolated value.

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DIELECTRIC CONSTANT, POWER FACTOR, AND RESISTIVITY OF MARBLE

By Arnold H. Scott

ABSTRACT

The dielectric constant, power factor, and resistivity of marble from Vermont, Alabama, and Georgia were determined when the marble was dry and after it had been stored for over a month in an atmosphere having a relative humidity of 85 percent. The effect of frequency on the dielectric constant and power factor was also studied. The results are presented in the form of tables. It was found that the electrical properties of marble may vary widely but that the colored marbles have higher dielectric constants and power factors than the white marbles.

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I. INTRODUCTION

Data on the electrical properties of marble are meager. Such data as are published vary widely. To gain more information regarding the electrical properties of marble, measurements of dielectric constant, power factor, and resistivity were made on specimens which were available from quarries in Vermont, Alabama, and Georgia. The effects of moisture and frequency on these electrical properties were studied.

II. DESCRIPTION AND PREPARATION OF SPECIMENS

The specimens were disks of marble about 7 mm thick and 15 cm in diameter, cut from slabs which had been carefully selected as to uniformity of appearance and coloring. The surfaces of these slabs had been carefully ground and polished.

Three varieties of marble were obtained from Vermont. These were designated as "White Vermont," "Blue Vermont," and "Jetmar." The White Vermont specimens were pure white. The Blue Vermont specimens were blue gray with darker patches or streaks giving a mottled, or clouded, appearance. The Jetmar specimens were specimens of blue-gray marble which had been impregnated with a bituminous material to give it a uniform black color.

The marble obtained from Alabama consisted of two varieties, which were designated "White Alabama" and "Clouded Alabama." The White Alabama specimens were pure white, while the Clouded Alabama specimens were white with bluish areas or streaks, which gave them a clouded appearance.

The marble obtained from Georgia was all of one kind. These specimens had a bluish-gray color and the grain of them was much larger than the grain of the Vermont and Alabama marbles.

Electrical measurements were made under two conditions of moisture content. After the specimens had been cut to the proper size, they were dried for 24 hours in an oven at 150° C and then kept in a desiccator until electrical measurements were made. Following these measurements, some of the specimens were put in the humidity chamber, in which the relative humidity was maintained at 85 percent. After a little more than a month in this chamber, the specimens were again measured.

Mercury electrodes were used for the resistivity measurements and tinfoil electrodes for the dielectric-constant and power-factor measurements. The mercury electrodes were applied as described by Curtis.[1] The tinfoil electrodes were applied with a thin coat of petrolatum. They were rolled down with a narrow roller until no further mark could be made on the foil with the roller. The tinfoil was applied over the entire area of each flat surface; then one of the electrodes was cut with a circular cutter and a narrow ring removed, leaving a circular electrode with a guard electrode surrounding it. The diameter of the center, or guarded, electrode was 11.0 cm, and the width of the gap between the guarded electrode and the guard ring was about 0.05 cm.

III. DESCRIPTION OF ELECTRICAL MEASUREMENTS

The volume resistance of each specimen was measured by the direct-deflection method described in a former paper.[2] For these measurements the specimens were at room temperature.

The dielectric-constant and power-factor measurements were made as described in another paper.[3] The specimens were mounted in a metal box which was part of a constant-humidity chamber and which was kept at a temperature of 25° C. This metal box served as an electrostatic shield and was so designed that all stray capacitance was removed from the measuring circuit. The capacitance and power factor were measured with a conjugate Schering bridge with an earthing arm.[4] A vibration galvanometer was used as detector at 100 c/s in connection with a one-stage amplifier. At 1,000 c/s the vibration galvanometer was replaced by a telephone receiver. For frequencies above 1,000 c/s an amplifier was used which had an oscillator built into it so that a 1,000-cycle beat note was produced. A telephone receiver was then used to detect the beat note.

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[4] This bridge is described in a tentative method of the ASTM entitled "Tentative methods of testing electrical insulating material for power factor and dielectric constant, D 150-36T." See Proc. Am. Soc. Testing Materials **36**, pt. 1, 955 (1936).

IV. RESULTS

The results of the different measurements are given in tables 1 to 4. The maximum, minimum, and mean values are given for each variety of specimens and for each set of given conditions. The conditions which were varied were the amount of absorbed moisture and the frequency of the alternating current used in measuring the dielectric constant and power factor.

TABLE 1.—*Dielectric constant of marble at 1,000 cycles per second*

Variety of marble	Dry				After 30 days at 85-percent relative humidity				
	Number of specimens	Maximum	Minimum	Mean	Number of specimens	Maximum	Minimum	Mean	Percentage of increase
White Vermont	4	8.64	8.55	8.58	3	9.41	9.04	9.21	7
White Alabama	4	8.57	8.55	8.56	4	8.71	8.60	8.67	1
Blue Vermont	8	8.80	8.62	8.72	4	9.78	8.94	9.31	6
Clouded Alabama	8	9.05	8.66	8.83	4	11.36	9.93	10.41	17
Jetmar	4	8.40	8.34	8.38	4	8.60	8.42	8.49	1
Georgia	8	10.55	10.03	10.32	3	14.08	13.22	13.69	35

TABLE 2.—*Power factor of marble at 1,000 cycles per second*

Variety of marble	Dry				After 30 days at 85-percent relative humidity				Ratio, moist/dry
	Number of specimens	Maximum $\times 10^3$	Minimum $\times 10^3$	Mean $\times 10^3$	Number of specimens	Maximum $\times 10^3$	Minimum $\times 10^3$	Mean $\times 10^3$	
White Vermont	4	1.2	1.0	1.1	3	40	25	33	30
White Alabama	4	5.6	2.5	3.4	3	14	3	9	3
Blue Vermont	8	8.3	3.0	4.7	4	53	19	32	7
Clouded Alabama	8	14.0	3.5	8.6	4	310	160	230	27
Jetmar	4	2.7	2.3	2.5	4	13	3	5	2
Georgia	8	31.0	11.0	18.0	3	230	170	200	11

TABLE 3.—*Volume resistivity of marble*

Variety of marble	Dry				After 30 days at 85-percent relative humidity				Ratio, dry/moist
	Number of specimens	Maximum ohm-cm	Minimum ohm cm	Mean ohm-cm	Number of specimens	Maximum ohm-cm	Minimum ohm-cm	Mean ohm-cm	
White Vermont	4	24×10^{13}	21×10^{13}	22×10^{13}	2	1.3×10^{13}	1.2×10^{12}	1.3×10^{13}	20
White Alabama	4	340	20	180	4	0.054	0.005	0.024	8,000
Blue Vermont	6	1,800	50	630	3	.18	.04	.11	6,000
Clouded Alabama	8	300	20	140	8	.10	.005	.031	5,000
Jetmar	4	4,700	2,600	3,900	4	1,800	9	1,000	4
Georgia	8	1,200	50	380	8	.64	.007	.20	2,000

TABLE 4.—*Change of dielectric constant and power factor of dry marble with frequency*

Frequency	Variety of marble			
	White Vermont		Blue Vermont	
	Dielectric constant	Power factor	Dielectric constant	Power factor
c/s				
100	8.60	1.4×10^{-3}	8.79	3.1×10^{-3}
1,000	8.58	1.1	8.75	4.2
10,000	8.57	1.7	8.69	5.0
50,000	8.55	1.6	8.65	4.8
100,000	8.53	1.4	8.63	

The values of the dielectric constant at 1,000 c/s are given in table 1. When measured dry, the dielectric constants of the White Vermont and White Alabama marbles may be considered as identical, since the indicated difference is less than experimental variation. However, when exposed to a relative humidity of 85 percent, the dielectric constant of the White Vermont marble increased more than the dielectric constant of the White Alabama marble.

The colored marbles had higher dielectric constants than the white marbles. Also, the moisture affected the dielectric constants of the colored marbles more than it did the dielectric constant of the White Alabama marble. The dielectric constants of the White Vermont and the Blue Vermont were about equally affected by moisture. On the other hand, Jetmar, which was artificially colored by impregnating with a bituminous material, actually had a lower value of dielectric constant than the white marble. Moisture affected the dielectric constant of Jetmar only slightly. This was to be expected as the bituminous material tended to make the marble moisture-repellent.

The values of the power factor at 1,000 c/s are given in table 2. There is a large spread between extreme values, in one case the maximum being 4 times the minimum. The colored marbles have higher power factors than the white marbles, and the moisture affects the power factors of the colored marbles more than it does the power factor of the White Alabama marble. However, the moisture increased the power factor of the White Vermont marble more than it did that of any of the other marbles. In a general way, the moisture affected the dielectric constants and power factors alike, that is, those specimens having large changes in dielectric constant also had large changes in power factor.

The values of volume resistivity are given in table 3. The spread between the maximum and minimum values is greater than for power factor. In one case the maximum is 200 times the minimum. There is no discernible systematic relationship between the values. The resistivities of the dry specimens are four to 10,000 times the resistivities of the moist specimens. There is no apparent connection between the resistivities and the power factors.

The change of the electrical property with absorbed moisture may not be that indicated by the change in mean values. In one case the

specimen which had a minimum value of power factor when dry had the maximum value of power factor when moist. In other cases it was the reverse.

The effect of frequency on the dielectric constant and power factor of dry marble is shown in table 4. Each of the values given is the average of measurements on four specimens. The dielectric constant decreased slightly with frequency, but there was no certain change of the power factor with frequency.

V. RESULTS OF PREVIOUS OBSERVERS

The values of the dielectric constant of marble obtained by other observers are given in table 5. The values given in this paper are consistent with these values. However, the work of Jaeger and of Preston and Hall indicates that the dielectric constant does not change with frequency, whereas the results of Rubens would indicate that the dielectric constant of marble increases with frequency. The present work, on the other hand, indicates that the dielectric constant decreases slightly with frequency.

The values of the resistivity of marble given by Curtis [5] were all much lower than the values given in this paper. He gave the value of 1×10^{9} ohm-cm for blue Vermont marble, 5×10^{9} ohm-cm for pink Tennesse marble and 1×10^{11} ohm-cm for Italian marble. These values were obtained at relative humidities encountered in the laboratory (probably below 35 percent), yet they are lower than the values given in table 3 at a relative humidity of 85 percent. As two of the specimens measured by Curtis were still available in the laboratory, they were remeasured. These measurements checked the previous measurements within the experimental error.

TABLE 5.—*Values of dielectric constant of marble obtained by previous observers*

Variety of marble	Dielectric constant	Frequency	Observer
		c/s	
Unknown	8.35	"Very high"	Schmidt.[1]
Do	8.35	250 to 10^{7}	Jaeger.[2]
Do	8.22	3×10^{7}	Rubens.[3]
Do	8.44	5×10^{9}	Do.[3]
Do	8.67	10^{13}	Do.[3]
White	9.3	8×10^{4} to 1.8×10^{6}	Preston and Hall.[4]
Gray	11.6	1.8×10^{6}	Do.[4]
Blue	9.4	1.8×10^{6}	Do.[4]

[1] W. Schmidt, Ann. Physik **11**, 114 (1903).
[2] R. Jaeger, Ann. Physik **53**, 409 (1917).
[3] H. Rubens, Sitzber. preuss. Akad. Wiss. p. 4 (1915); p. 556 (1917).
[4] J. L. Preston and E. L. Hall, QST **9**, 26 (Feb. 1925).

Kessler [6] has published values of volume resistivity for American marbles which ranged from 10^{6} ohm-cm to 3.9×10^{14} ohm-cm. The measurements were made on specimens which had been dried in air after immersion for 48 hours in water.

[5] Harvey L. Curtis, Bul. BS **11**, 359 (1914) S234.
[6] D. W. Kessler, *Physical and chemical tests on the commercial marbles of the United States*. Tech. Pap. BS **12** (1919) T123.

VI. CONCLUSIONS

It is apparent that the electrical properties of marble may vary widely. The colored specimens had higher dielectric constants and power factors than the white specimens. The resistivity varied so that general conclusions could not be drawn regarding it. Absorbed moisture increased the dielectric constant and power factor and decreased the resistivity. The variation between specimens was much greater for the moist specimens than for the dry. Because of the large variations between the values for different specimens and between different varieties, it is not possible to give definite values of the electrical properties of marble.

WASHINGTON, January 8, 1940.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1282

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REDUCING POWERS OF VARIOUS SUGARS WITH ALKALINE COPPER-CITRATE REAGENT

By Horace S. Isbell, William W. Pigman, and Harriet L. Frush

ABSTRACT

Scales' method for the determination of reducing sugars was modified by increasing the boiling time, and reducing values of 32 sugars were determined at various concentrations. The method as modified provides a very simple, convenient means for the quantitative determination of the various sugars. A comparison of the reducing values of different sugars reveals that the configurations of carbons 3, 4, and 5 have marked effect on the reducing values, but that the configuration of carbon 2 has little influence. Sugars in which the hydroxyl on carbon 3 is *trans* to the hydroxyls on carbons 4 and 5 have the highest reducing powers, while those which have *cis* hydroxyls on carbons 3 and 4 have lower reducing values. When the glycosidic union of a disaccharide is on carbon 3, the molecular reducing power is less than that of the monosaccharide corresponding to the reducing part of the molecule; if the glycosidic union is on carbon 4, the molecular reducing power is about 1.4 that of the corresponding monosaccharide, and if on carbon 6, the molecular reducing power is about 1.2 that of the corresponding monosaccharide. The effect of barium bromide on the reducing powers of the sugars varies with the experimental conditions. Under the conditions used in this investigation the presence of 6.5 percent of barium bromide lowers the reducing value by approximately 4 percent.

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I. CHARACTERISTICS OF THE METHOD

In the course of an investigation conducted in this laboratory [1, 2] [1] on the oxidation of the sugars, it was necessary to adopt a method for determining reducing sugars which is simple and requires relatively small samples. These requirements are met by a method described by Scales, in which the cuprous oxide formed by the reduction of alkaline copper-citrate reagent is titrated with iodine [3, 4]. According to the original method the sugar solution (10 ml) is mixed with 20 ml of the copper reagent, brought to boiling in 4 minutes, and boiled for 3 minutes. After cooling the solution, aqueous acetic acid, an excess of

[1] Figures in brackets indicate the literature references at the end of this paper.

0.04 *N* iodine, and aqueous hydrochloric acid are added. The excess iodine is then titrated with sodium thiosulfate. According to Scales, each milliliter of 0.04 *N* iodine is equivalent to approximately 1.12 mg of dextrose. In our experience the value depends slightly on the concentration, so that it is necessary to use factors which vary with the amount of sugar in the sample. The factor, or sugar equivalent, is merely the number of milligrams of anhydrous sugar corresponding to 1 ml of 0.04 *N* iodine under the conditions of the measurement.

When the method as described by Scales was applied to certain sugars in the presence of barium bromide, small variations in the boiling time gave erratic results. This appeared to be due to incomplete reduction caused by the retarding effect of barium bromide on the reaction. The difficulty was largely overcome by increasing the time of boiling to 6 minutes. Even when barium bromide is not present, the longer boiling time (especially for certain sugars) gives more uniform results. Notwithstanding this improvement, variations in the technique used in cooling the reduced copper solution and in adding the reagents affect the titration, so that different workers obtain slightly different factors. For this reason each investigator should determine his own factors whenever possible by following the same procedure with known quantities of the sugar under investigation.

Table 1 shows the variation of the dextrose factor with size of sample. Measurements were made according to the method described on page 245, by three different observers, each of whom made three determinations at each concentration. Application of the "least-squares principle" to the data given in table 1 gives the following equation:

$$f=1.0511+0.0021\ C+0.000086\ C^2, \tag{1}$$

in which f is the factor for glucose and C is the titration in milliliters of 0.04 *N* iodine solution.

These measurements and the measurements with other sugars, given in table 2, clearly show that the reducing power changes with concentration and that different factors must be used for different quantities of sugar.

TABLE 1.—*Variation of dextrose factors with samples of different sizes*

Milligrams of dextrose	Milliliters of 0.04 *N* iodine solution	Sugar factors				
		Observer			Average	Calculated from eq 1
		A	*B*	*C*		
5	4.69	1.078	1.066	1.055	1.067	1.063
10	9.30	1.078	1.074	1.073	1.075	1.078
15	13.72	1.101	1.096	1.083	1.093	1.096
20	17.92	1.123	1.115	1.110	1.116	1.116
25	21.93	1.146	1.148	1.127	1.140	1.139

TABLE 2.—*Factors for various sugars for use with the modified Scales method*[1]

Sugar	Milligrams of anhydrous sugar per milliliter of 0.04 *N* iodine				Sugar	Milligrams of anhydrous sugar per milliliter of 0.04 *N* iodine			
	5-ml titer	10-ml titer	15-ml titer	20-ml titer		5-ml titer	10-ml titer	15-ml titer	20-ml titer
l-Arabinose	1.078	1.092	1.107	1.127	Lactose	1.426	1.434	1.445	1.462
Cellobiose	------	1.383	1.393	1.413	Lactulose	1.460	1.467	1.477	------
d-Fructose	1.040	1.050	1.078	1.097	*d*-Lyxose	------	0.994	1.006	1.024
l-Fucose	------	1.201	1.235	------	Maltose	1.479	1.471	1.485	1.497
d-Galactose	1.215	1.223	1.240	1.267	*d*-α-Mannoheptose	------	1.310	1.328	------
d-α-Galaheptose	------	1.261	1.292	------	*d*-β-Mannoheptose	------	1.312	1.329	------
d-β-Galaheptose	------	1.259	1.283	------	*d*-Mannose	1.075	1.087	1.103	1.126
Gentiobiose	------	1.717	1.731	1.755	Melibiose	1.747	1.757	1.769	------
d-α-Glucoheptose	------	1.291	1.313	------	Neolactose	1.427	1.433	1.440	1.451
d-β-Glucoheptose	------	1.318	1.341	------	*l*-Rhamnose	------	0.973	0.999	------
d-Glucoheptulose	------	1.287	1.322	------	*d*-Ribose	1.049	1.065	1.083	1.106
d-Glucose	1.067	1.075	1.093	1.116	*l*-Sorbose	------	1.171	1.182	------
4-β-Glucosido-mannose	------	------	1.360	1.392	*d*-Talose	------	1.224	1.240	------
d-α-Guloheptose	------	1.291	1.312	------	Turanose	------	2.691	2.714	------
d-β-Guloheptose	------	1.318	1.341	------	*d*-Xylose	0.996	1.007	1.021	1.040
d-Gulose	------	1.152	1.170	------	Invert sugar	1.061	1.067	1.082	1.095

[1] The factors given in this table are the averages of the values obtained in measurements conducted in this laboratory over a period of 8 years. Each value represents not less than 3 determinations. The individual determinations by the same operator did not vary over 1 percent, but the results of different operators varied by as much as 2 percent.

II. RELATIONS BETWEEN STRUCTURE, CONFIGURATION, AND REDUCING POWER

The reducing values obtained with asymmetric reagents, such as the copper *d*-tartrate solution, depend on the configuration of the reagent as well as on the configuration of the sugar and differ for enantiomorphic sugars [5, 6]. Since the alkaline copper-citrate reagent does not contain an asymmetric substance, it gives like reducing values for enantiomorphic isomers, and is particularly suitable for studying the relationship between configuration and reducing power. Since copper reagents buffered with sodium carbonate and bicarbonate oxidize the sugars more slowly than those containing sodium hydroxide [7], the reducing values depend upon the copper reagent used and upon the experimental conditions. The relative reducing powers observed for a series of sugars under one set of conditions with one reagent may differ widely from those found under different conditions with another reagent.

The various sugars under strictly comparable conditions reduce different quantities of copper. It may be observed by comparing the reducing values given in table 3 that epimeric sugars give approximately like reducing values—that is, the configuration of carbon 2 does not materially influence the reducing power. The similarity of epimeric sugars probably arises from the rapidity with which they revert to the common enolic form. Since the groups about carbons 3, 4, and 5 are held more firmly, sugars which differ in the configuration of these carbons are not interconvertible in the alkaline solution and exhibit characteristic properties. Sugars in which the hydroxyl on carbon 3 is *trans* to the hydroxyls on carbons 4 and 5 give the highest reducing powers, while sugars which have *cis* hydroxyls on carbons 3 and 4 give lower reducing values. The differences in the values for lactose, maltose, cellobiose, and turanose show that the configuration of the nonreducing component in the disaccharide

molecule influences the reducing power and that the reducing power of the disaccharide may be higher or lower than that of the reducing sugar component. If the glycosidic union is on carbon 3, as in turanose, the molecular reducing power is less than that of the corresponding monosaccharide. If the glycosidic union is on carbon 4, the molecular reducing power is about 1.4 that of the corresponding monosaccharide; and if the glycosidic union is on carbon 6, the molecular reducing power is about 1.2 that of the corresponding monosaccharide. It may be observed from the results given in table 4 that the molecular reducing powers of the pentoses are slightly lower and of the heptoses slightly higher than the molecular reducing powers of the corresponding hexoses.

TABLE 3.—*Relative molecular reducing powers* [1] *(modified Scales method)*

Sugar	Sample: anhydrous sugar in 10 ml	0.04 *N* iodine solution consumed by Cu_2O	Relative molecular reducing powers: glucose=1
	mg	*ml*	
d-Glucose	15	13.7	1.00
d-Mannose	15	13.6	0.99
d-Fructose	15	13.9	1.01
l-Rhamnose	13.7	13.8	1.01
d-Galactose	15	12.2	0.89
d-Talose	15	12.2	.89
l-Fucose	13.7	11.4	.83
d-Gulose	15	12.9	.94
l-Sorbose	15	12.8	.93
l-Arabinose	12.5	11.4	.83
l-Ribose	12.5	11.7	.85
d-Ribose	12.5	11.7	.85
d-Xylose	12.5	12.4	.91
d-Lyxose	12.5	12.6	.92
d-α-Galaheptose	17.5	13.6	.99
d-β-Galaheptose	17.5	13.7	1.00
d-α-Glucoheptose	17.5	13.6	0.99
d-β-Glucoheptose	17.5	13.1	.96
d-Glucoheptulose	17.5	13.3	.97
d-α-Mannoheptose	17.5	13.2	.96
d-β-Mannoheptose	17.5	13.2	.96
d-α-Guloheptose	17.5	13.4	.98
d-β-Guloheptose	17.5	13.1	.96
4-β-Glucosido-mannose	28.5	20.4	1.49
4-β-Glucosido-glucose (cellobiose)	28.5	20.2	1.47
4-α-Glucosido-glucose (maltose)	28.5	19.1	1.39
4-β-Galactosido-glucose (lactose)	28.5	19.5	1.42
4-β-Galactosido-fructose (lactulose)	28.5	19.1	1.39
4-β-Galactosido-altrose (neolactose)	28.5	19.7	1.44
6-β-Glucosido-glucose (gentiobiose)	28.5	16.4	1.20
6-α-Galactosido-glucose (melibiose)	28.5	16.1	1.18
3-α-Glucosido-fructose (turanose)	28.5	10.6	0.77

[1] Ratio of the reducing power of the sugar to the reducing power of glucose.

TABLE 4.—*Molecular reducing powers for configurationally related substances*

Configuration [1]				Average molecular reducing power		
C_2	C_3	C_4	C_5	Pentoses	Hexoses	Heptoses
+	−	+	+	0.91	1.00	1.00
−	−	+	+	.92	0.99	0.99
+	−	−	+	.83	.89	.96
−	−	−	+	.85	.89	.96
+	+	−	+	--------	.94	.99
−	+	−	+	--------	--------	.96

[1] The configurations of carbons 2, 3, 4, and 5 are indicated by plus and minus signs according to whether the OH lies to the right or left when the formula is written in the conventional manner. For example, the configuration of *d*-glucose is indicated by + − + +. In the case of the pentoses, the sugar has been classified with the configurationally related hexose. Thus *d*-xylose, *d*-lyxose, *l*-arabinose, and *l*-ribose are placed with groups having the (+) configuration for carbon 5.

III. EFFECT OF BARIUM BROMIDE ON THE REDUCING POWER

In harmony with prior observers, who noted that barium and calcium salts alter the reducing power of certain sugars, we found that the addition of either barium bromide or calcium chloride results in a marked decrease in the reducing power. The effect of barium bromide on the reducing power is shown by the data given in table 5, which was compiled from the results obtained in the course of our studies on the oxidation of the sugars with bromine water. Under the conditions of our measurements, and depending to some extent on the concentration of the sugar, the presence of 6.5 percent of barium bromide in the sugar solution lowers the reducing values by approximately 4 percent. If the time of boiling or any other experimental condition is altered, the effect may be larger or smaller.

TABLE 5.—*Effect of barium bromide on the reducing values obtained by the modified Scales method*

Sugar	Ratios of reducing values [1] for 10-ml samples containing—			
	10 mg of sugar; 0.317 g of $BaBr_2$	20 mg of sugar; 0.317 g of $BaBr_2$	10 mg of sugar; 0.656 g of $BaBr_2$	20 mg of sugar; 0.656 g of $BaBr_2$
d-Glucose	0.982	0.987	0.954	0.958
d-Mannose	.979	.987	.949	.960
l-Rhamnose	.983	.989	.958	.967
d-Galactose	.981	.981	.957	.957
d-Talose	.981	.984	.946	.957
l-Fucose				.967
d-Gulose	.979	.986	.955	.961
d-Arabinose	.987	.989	.956	.961
l-Arabinose				
l-Ribose	.975	.979	.936	.948
d-Ribose				
d-Xylose	.977	.982	.942	.955
d-Lyxose	.974	.988	.941	.957
d-α-Galaheptose	.982			
d-β-Galaheptose	.980			
d-α-Glucoheptose	.974			
d-β-Glucoheptose	.965			
d-α-Mannoheptose	.988			
d-β-Mannoheptose	.980			
d-α-Guloheptose	.982			
d-β-Guloheptose	.985			
	30 mg of sugar; 0.317 g of $BaBr_2$	30 mg of sugar; 0.656 g of $BaBr_2$		
1-α-Glucosido-glucose (maltose)	0.990	0.972		
1-β-Galactosido-glucose (lactose)	.987	.965		
1-β-Glucosido-mannose		.958		
6-β-Glucosido-glucose (gentiobiose)	.982	.957		
6-α-Galactosido-glucose (melibiose)	.973	.949		
1-β-Galactosido-altrose (neolactose)	.982	.969		

[1] The ratio of the reducing value of the sugar in the presence of barium bromide to the reducing value of the sugar under like conditions in the absence of barium bromide.

IV. METHOD FOR MAKING SUGAR DETERMINATIONS

Reagents needed:

1. Alkaline copper-citrate reagent. Dissolve 16 g of copper sulfate ($CuSO_4 \cdot 5H_2O$) in 125 to 150 ml of water. Dissolve 150 g of sodium

citrate ($2Na_3C_6H_5O_7 \cdot 11H_2O$),[2] 130 g of anhydrous sodium carbonate, and 10 g of sodium bicarbonate in about 650 ml of water, while warming them slightly to accelerate solution. Combine the two solutions with stirring, make up to 1 liter, and filter.

2. 0.04 *N* solution of iodine containing 4 percent of potassium iodide.

3. 0.04 *N* sodium thiosulfate solution containing 0.1 g of sodium carbonate.

4. Hydrochloric acid solution containing 60 ml of concentrated HCl per liter.

5. Acetic acid solution containing 24 ml of glacial acetic acid per liter.

Procedure:

To 10 ml of a solution containing 10 to 20 mg of a monosaccharide (or about 30 mg of a disaccharide) and contained in a 300-ml Erlenmeyer flask, add from a fast-draining pipette 20 ml of the copper reagent.[3] Stopper the flask with a two-hole rubber stopper and place over an electric heater so regulated that the solution comes to boil in $4 \pm \frac{1}{4}$ minutes. Allow the solution to boil for 6 minutes and then cool it in an ice-water bath for ¾ minute while keeping the solution in gentle circular motion.[4] Remove the flask from the ice-water bath, draw up 25 ml of 0.04 *N* iodine solution into a pipette, and while holding the pipette, pour into the flask from a graduate 100 ml of the acetic acid solution, mix gently, and add the iodine solution from the pipette. Then pour 25 ml of the hydrochloric acid solution down the walls of the flask and into the solution. Mix with a gentle circular motion and titrate the excess iodine with 0.04 *N* sodium thiosulphate, using starch as the indicator.[5] Subtract the back titration from the iodine originally added and multiply this value by the sugar factor to give the milligrams of sugar in the sample. For best results each worker should determine his own factors by applying the method to known quantities of sugars. If a large number of determinations is to be made, charts in which the factors are plotted against the titrations may be constructed so that the factor for any titration may be obtained readily.

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WASHINGTON, January 5, 1940.

[2] If $Na_3C_6H_5O_7 \cdot 2H_2O$ is used, 124 g should be taken.

[3] The amount of sugar in the sample should be such that there is still an excess of the alkaline copper reagent after the oxidation.

[4] For heating the samples a conical electric heater with all rings removed, and covered with an asbestos-centered wire gauze is recommended. It is connected in series with an adjustable resistance. A cylindrical shield should be placed around the flask during heating in order to protect it from drafts. When a number of determinations are to be made, a flask containing another sample may be placed on the electric heater as soon as the preceding sample has been removed. The time of heating is sufficient to allow for the titrations and for preparation of the next sample.

[5] The iodine solution added should be at least 4 ml in excess. Before the excess iodine is titrated, the cuprous oxide precipitate must all be in solution. Because of the equilibrium between the iodide, cuprous, and cupric ions, it is necessary to follow the directions closely.

U. S. Department of Commerce National Bureau of Standards

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MEASUREMENT, IN ROENTGENS, OF THE GAMMA RADIATION FROM RADIUM BY THE FREE-AIR IONIZATION CHAMBER

By Lauriston S. Taylor and George Singer

ABSTRACT

The free-air ionization chamber is the accepted standard for calibrating X-ray dosage measuring instruments. With the advent of supervoltage X-rays, the need for proved standards for this range has arisen.

The present paper describes an investigation of the applicability of the free-air pressure ionization chamber for measuring radiation at the high-frequency end of the X-ray spectrum, that of the gamma radiation from radium.

Measurements were made with a narrow collimated beam of gamma rays at pressures up to 10 atm. Because of inability to obtain full current-voltage saturation, application was made of the extrapolation of reciprocal current-voltage curves in accordance with the Jaffe-Zanstra theory. This was first tested carefully with 350-kv X-rays at 1-, 6-, and 10-atm pressure and found to hold within our experimental limits. It was found that at 10-atm pressure a plate separation of about 35 cm is necessary to utilize the full electron range. Ranges in the forward direction were not effectively greater than 70 cm. Measurements of the gamma-ray emission from radium gave a value of 8.16 roentgens per milligram per hour at a distance of 1 cm, which is in line with several similar determinations by other methods.

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I. INTRODUCTION

The free-air [1] ionization chamber is the accepted standard for calibrating X-ray dosage-measuring instruments. With the advent of million-volt X-rays, the need for proved standards for this range has

[1] A "free-air" ionization chamber is one wherein the volume from which the ions are effectively measured is surrounded by an envelope of air having a thickness in all directions at least as great as the maximum range of the secondary electrons entering or leaving the volume in those directions. For low voltages the ionization chamber is usually used with air at atmospheric pressure and is frequently termed an "open-air" ionization chamber. In this paper the use of the term "free air" is extended to those chambers operating with air at elevated pressures.

arisen. In a recent publication [1] [2] the application of the free-air ionization chamber, with certain pertinent modifications in technique and necessary precautions, was described, in which was proved the adequacy of the free-air chamber for measuring X-rays up to 400-kv excitation potentials. This work still leaves its application to the higher frequency radiation untested.

Equipment is under construction to extend this investigation to 1,400 kv. In the meantime, the applicability of the methods has been investigated by studying ionization produced by gamma rays of radium. These rays comprise radiations ranging from 600 to 2,000 kv, roughly comparable to 1,500-kv X-rays. The ionization produced at unit distance from 1 mg of radium is an important physical quantity, uncertainties in which arise largely from experimental difficulties inherent in realizing the definition of the roentgen for very high frequency radiations. The measurement of X-rays and gamma rays by means of the same instrument and procedure lends greater confidence to the expression of X- and γ-ray dosages in a common unit—the roentgen.

The ionization produced by a narrow collimated beam of gamma rays in an air ionization chamber at pressures up to 10 atm has been measured. The investigation involved:

1. A study of the dimensions and pressures required to eliminate wall effects. This involved a study of the general ionization-chamber design with particular respect to the plate spacings and diaphragm-collector distances at various air pressures so as to insure a state of full electronic equilibrium. It also included an investigation of the diaphragming and collimating system necessary to the unambiguous measurement.

2. A determination of the correction for columnar recombination and lack of saturation. Current-voltage saturation conditions were studied, and Jaffes' theory of columnar ionization was applied to determine the saturation current.

3. A determination of the fraction of the total gamma radiation reaching the ionization chamber. This involved a review of the fundamental calibration methods for radium preparations, with relation to the measurements of the emission constant of radium in accordance with the definition of the roentgen. Included in this were corrections for the absorption of the gamma rays in air, platinum, and the radium salt itself.

Finally, the various experimental results were applied to an evaluation of the emission constants of radium in roentgens. After an analysis of the various errors involved, the results were compared with similar determinations by other methods.

The use of a relatively large quantity of radium facilitated measurements at low current sensitivities and for satisfactory distances, so that quantities involving these measurements could be evaluated with high accuracy and permit the more ready localization of any other errors.

This work was made possible through the cooperation of the National Institute of Health, which lent us, for the purpose, a specially made platinum cylinder containing about one-half gram of radium.

[2] Figures in brackets indicate the literature references at the end of this paper.

II. HIGH-AIR-PRESSURE IONIZATION CHAMBER

The ionization chamber employed in this investigation has been described in detail [1] in connection with supervoltage X-ray investigations, no changes having been made for this study. Briefly, it consists of a guarded-field parallel-plate chamber (75 cm long with a maximum plate separation of about 40 cm) placed in a steel pressure tank 8 ft long and 2½ ft in diameter, suitable for operating normally up to 10 atm and, if needed, at double that pressure. Plate separation and position along the axis of the cylinder are adjustable from without through suitable airtight joints. An aluminum "window" 1.0 mm thick and 6 cm in diameter permits the effectively unobstructed entry of the radiation beam.

Air was supplied from a small compressor with intake passing through a large calcium chloride dryer, and outlet through a cylinder packed with rag waste to absorb any oil vapor or other foreign matter from the pump. Several canisters of calcium chloride dryer were also placed in the tank to remove any final traces of moisture, so that all measurements could be made under dry-air conditions.

Up to about 4 atm, the pressure was measured with a multiple-tube mercury manometer [2] to an accuracy of ± 0.1 percent. At higher pressures a Bourdon gage, calibrated with a piston gage to an accuracy of ± 0.3 percent at the particular gage points of the study, was used.

Saturation voltage was supplied from either of two sources, depending upon the magnitude of field required and the electrometer system employed. With the more sensitive vacuum-tube electrometer, very small fluctuations in the saturating voltage induced large deflections of the galvanometer. By test, it was found that fluctuations in the plate voltage exceeding ± 0.01 volt were intolerable; consequently, where plate voltages of 10,000 are used, a steadiness of 1 part in 10^6 is required and 1 part in 10^7 desirable.

For potentials up to 8,000 volts, heavy duty *B* batteries were employed. Although an individual cell is probably not steady to the required degree, the fluctuations of the 5,000 cells were statistically balanced and the resultant voltage was steady to 1 part in 10^8.

Above 8,000 volts, a valve rectifier-filter was required. Stabilization of these voltages within our required limits proved to be impracticable by any of the usual methods; our requirement that the output voltage be variable was one of the main difficulties. An attempt to use the manual-compensation method described by Pallister [3] showed it to be inadequate for our needs. Indirect compensation was finally accomplished through a modification of the Swann methods, whereby a definite fraction of the fluctuating plate voltage is applied to the electrometer grid circuit in such a way as to balance out the plate-voltage variations.[3] By this means, plate voltages up to 25 kv were available.

Careful tests were made for any possible corona or other leakage at these high plate voltages. At atmospheric pressure, corona hissing began at about 4,000 volts and break-down occurred at about 15 kv. Up to the latter point, there was no visible corona nor did any corona occur in regions such that it could be detected with our highest electrometer sensitivities. At 10 atm, tests up to 30 kv showed no break-

[3] This will be described elsewhere.

down or visible corona, nor was any leakage effect detected by the electrometer. It is interesting to note that after any prolonged pumping of air into the cylinder, the electrometer showed erratic deflections attributable to stray ions (or probably ion clusters) caused by the air friction. At times it required 24 hours' rest after pumping for this effect to completely disappear. Broxon and Meredith [4] found similar disturbances in their very much smaller system and sometimes allowed several days for "aging" of the air.

Current measurements were made by essentially the same means used in our earlier X-ray measurements [1]. For comparative current measurements, the ion current was balanced against a known current through a very high (S. S. White) resistor. For absolute measurements, the same electrometer system was used as a null detector in a capacitance compensator system [5].

In both comparative and absolute measurements, the current was read in terms of a known voltage applied across the resistor or capacitor. This voltage was adjusted and read directly on an L & N type *K* potentiometer with an accuracy far beyond our requirements.

The need for shielding from radiation around the electrometer and conductors was carefully investigated. The radiation field was considerably restricted by the strict shielding and collimation at the radium as described below.

The electrometer tube was placed in a lead cylinder (wall, one-fourth in.) which in turn was supported just outside the end of the pressure tank opposite to and about 10 ft from the radium. Under these conditions, and with a relatively large testing potential difference applied between the grid circuit and the shield, no ionization current was detectable at the highest sensitivities used. In normal operation there is practically zero potential difference between grid leads and case.

In the capacity compensating system the capacitor had an ionizable volume of about 20 cm^3 and was subject to a potential difference of several volts between plates. This, shielded by about 2 cm of lead shot, also showed no evidence of stray ionization between plates. A third electrometer-tube housing, having no lead shielding but capable of being evacuated, was also tested and the system found insensitive to radiation either at 760-mm or at 10^{-2}-mm pressure.

Statistical variations in ionization produced by the radium caused random fluctuations of the electrometer zero amounting to about 2 percent of the measured current when using the galvanometer employed in earlier studies. These fluctuations were reduced to a level of about 0.5 percent of the working deflection by increasing the galvanometer period, although the measurements were thereby made somewhat more laborious.

III. DIAPHRAGMS

For most comparative measurements the construction, thickness, and alinement of the diaphragm are not important so long as the open and closed positions are reproducible. For absolute measurements, however, the thickness must be sufficient to reduce the radiation leakage through the walls of the diaphragm to less than 0.1 percent of that through the orifice. To avoid the thick diaphragms necessary with radium, most workers have collimated the radiations

by imbedding the radium in a lead block at the bottom of a deep well with walls of requisite taper. This collimating arrangement, requiring the presence of some sort of shutter system, makes it somewhat difficult to properly evaluate the scattered and background radiation. In an endeavor to avoid this difficulty, as well as to retain a system suitable for measuring X-rays of very high voltage, a diaphragm arrangement was constructed on the same general principle as for the measurement of such X-rays.

A practice in the past has been to use diaphragms which were too thin and to make corrections by subtracting the reading made with

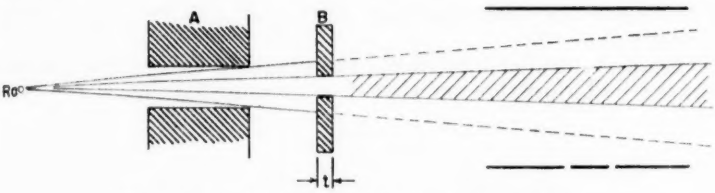

FIGURE 1.—*Diagram of thin-diaphragm system.*

the diaphragm closed from that made with the diaphragm open, thereby supposedly eliminating the background radiation. For radium, this procedure is not valid for the following reason: Take a gamma-ray beam partially limited by a lead block, *A* (fig. 1), and further by the limiting diaphragm, *B* of thickness *t*. With the aperture open, the total radiation measured is the unobstructed part passing through the aperture plus that which passes through the surrounding wall. With the aperture closed by a plug, the radiation measured is again that which passes through the wall plus that which

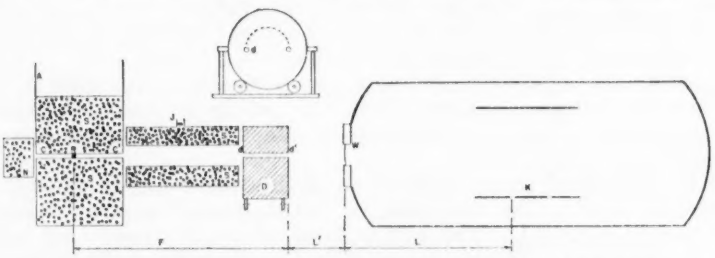

FIGURE 2.—*Diagram of thick diaphragm and collimating system.*

passes through the plug. The difference in the two measurements gives that passing through the aperture plus that which passes through the plug, and the result is consequently in error by the latter amount. This error is reduced by increasing the thickness *t*, of the diaphragm. Since, then, the resultant quantity is a function of the diaphragm thickness *t*, the thickness should be such that no appreciable amount of radiation passes through it.

The arrangement of the system finally adopted is shown diagrammatically in figure 2. *N* is a 5-in. lead screening cube (or box filled with 0.02-in. lead shot) mounted on rollers; *A* is an iron can (35-cm diam, 50 cm high) filled with lead shot in which is mounted, opposite appropriate windows, a thin copper tube, *cc'*, 10-mm inside diameter

for carrying the radium, *R; J* is a hollow cylinder having its 2½-in. wall filled with .02-in. shot; *D* is a brass tube (diam 6 in., length 6 in.) filled with solid lead through which is drilled an eccentrically placed orifice *dd'*, so that by rotation of *D* in its supporting saddle, the orifice can be either entirely open to, or completely shielded from the radiation from R; and finally, the pressure tank with aluminum window, *W*, and ionization chamber, *K*.

The limiting aperture *dd'* was formed by first drilling a commensurate hole and then forcing through it a series of plug gages which gradually enlarged the opening and burnished it accurately to size. The carrying saddle was on ball bearings and provided with stops which insured accurate repetition of "open" and "closed" positions, 180° apart.

To establish proper alinement, the aperture *dd'* was first adjusted in height and direction so that the transmitted beam would pass

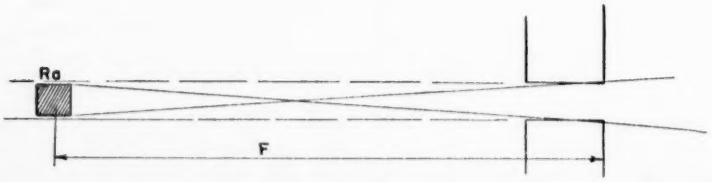

FIGURE 3.—*Diagram showing the passage of radiation through the edges of the diaphragm.*

centrally through the window, *W*, of the pressure tank and along the central axis of the ionization chamber. This adjustment was not at all critical. The plug gage finally used was then reinserted in *dd'*, fitting snugly and reaching through the radium carrier tube, *cc'*, which was then fixed in its position by filling the tank, *A*, with shot. The alinement of *J* simply required correct "open" and "closed" positions. On removing the plug gage, inserting the radium, and shifting the screen, *N*, into place, the set-up is ready for making measurements. The time required to effect this alinement does not exceed 15 minutes.

It is particularly important when dealing with highly penetrating radiations that in the operation of the shutters the stray radiation field is not changed. The rotary type of shutter here used fulfills this requirement. It was found that by using the collimating and screening system as described, the background radiation did not exceed 4 percent of that of the direct beam, and by inference, the error introduced by the quantity passing through the "plug" alone was negligible. This low background radiation was no doubt responsible for the low-shielding requirements around the electrometer system mentioned above.

With the type of collimating system here used, there will, of course, be a small amount of radiation transmitted through the edge of the diaphragm at the exit end of the orifice owing to the obliquity of the rays from the outer parts of the radium source (see fig. 3). The relative magnitude of this effect will decrease with increasing distance, F, between radium and diaphragm. Calculations were made for such leakage by dividing the exit face of the orifice into narrow concentric zones and then computing the transmission of each. The results given in table 1 are the maximum, and the actual transmission may possibly be less by as much as 10 percent. Since most of the other measurements were made at F=62.5 cm, a 2-percent correction only was applied.

TABLE 1.—*Transmission through edge of diaphragm in percentage of unobstructed radiation*

F	Percent
cm	
50	2.7
60	2.2
65	1.8
70	1.7
75	1.6

Since the thickness of the diaphram, dd', is not small compared to its distance from the source of radiation, and since its wall is not perfectly opaque, the question arises whether or not the aperture at d' is, as for the ideal case, the limiting aperture for determining the quantity of ionization. For ideal conditions and all radiant points sufficiently close to the axis of the system, and sufficiently close to a fixed distance from the end, d', the quantity of direct radiation passing through the diaphragm varies inversely as the square of the distance of the source from d'. The quantity of the radiation reaching the ionization chamber from the inner walls of the aperture is negligible, and that passing through the edges of the diaphragm is given in table 1. Of course, the radiation originates from an extended and not a point source; but as long as the diameter of the source is small compared to the distance, F, (1:70 in our case) and is smaller than the diaphragm diameter the inverse-square law may be expected to hold.

To test the question, ionization-chamber measurements on the transmitted radiation were made with the radium at a series of positions within its collimating tube, cc'; that is, at different distances, F, between the radium and the exit face, d', of the diaphragm. Corrections to these measurements were then made from table 1, and the results plotted against the inverse square of the distance—in figure 4. The plotted points fall very closely on a straight line through the origin and thus justify the assumption that the limiting aperture is at the exit face of the diaphragm; and also assure the practical correctness of the calculated magnitudes of table 1.

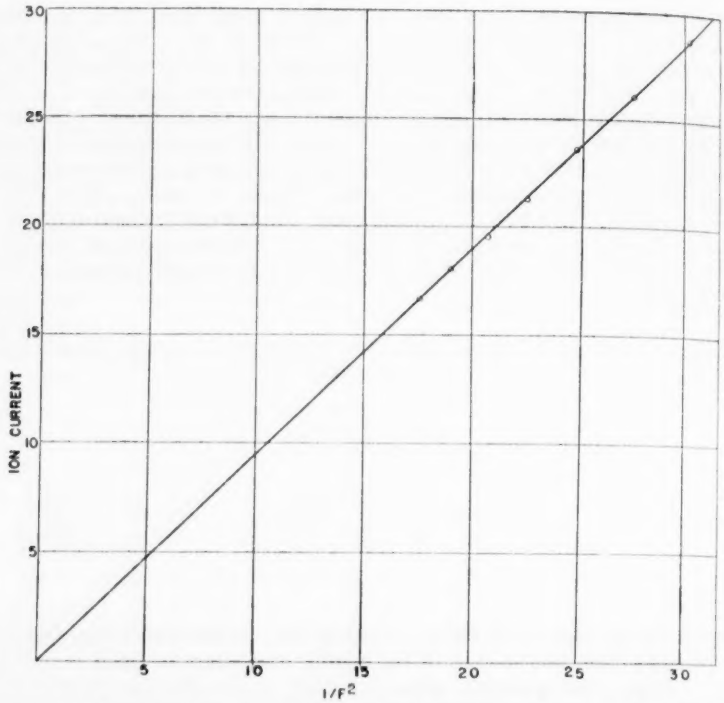

FIGURE 4.—*Inverse-square-law plot for distance between radium and diaphragm edge.*

IV. SATURATION

With the requisite plate spacing of about 30 cm and a pressure of 10 atm, saturation voltages are expected to be high, and in fact saturation is not completely obtainable because of columnar recombination at this pressure. Figure 5 shows a current-voltage curve of the ioniza-

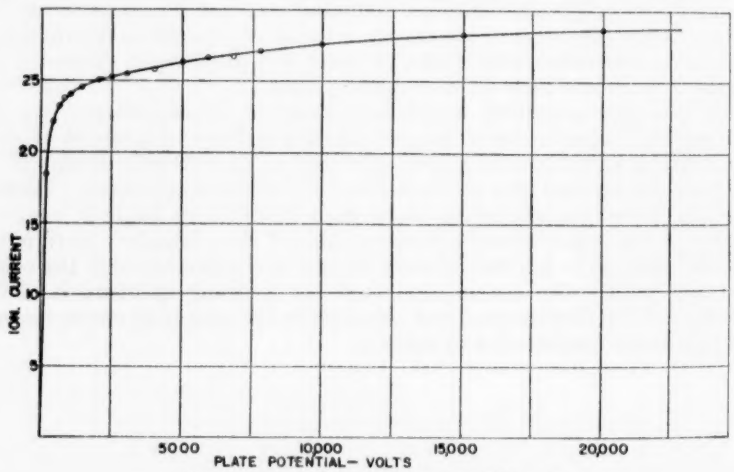

FIGURE 5.—*Saturation curve at 10 atm.*

tion chamber under such conditions. There is no evidence of saturation at the highest field strengths, 670 volt/cm, corresponding to the applied potential of 2×10^4 volts. This condition is expected because it corresponds to only 67 volt/cm at 1 atm, which is barely sufficient to produce saturation at that pressure, even neglecting columnar recombination. Applied potentials above 20 kv could not, however, be used because the resulting unsteadiness exceeded the permissible limits.

The possibility of applying Jaffe's theory of columnar ionization for extrapolating to saturation conditions was suggested by our earlier work on the X-ray ionization of liquids [6, 7, 8], and later work by Zanstra [9] and by Clay and coworkers [10, 11], who have applied it to gases from 20 to 400 atm. Their findings have been further verified by Broxon and Meredith [4] with high-pressure cosmic-ray ionization chambers.

Zanstra gives the following relation between the current, i, and the saturation current, I:

$$\frac{1}{i}=\frac{1}{I}+\frac{q}{I}f(x), \tag{1}$$

where

$$\frac{q}{I}=\frac{\alpha N_0}{8DI} \tag{1a}$$

in which N_0 is the number of ions per centimeter of path length, D is the diffusion coefficient, and α is the recombination coefficient. $f(x)$ is a Hankel cylinder function of the form

$$f(x)=e^x(j\pi/2)H_0^{(1)}(jx), \tag{2}$$

where

$$x=c\cdot\left(\frac{X}{p}\right)^2, \tag{3}$$

in which X is the field strength, p is the pressure in atmospheres, $j=\sqrt{-1}$, and for air, $c=1.24\times10^4$.

Figure 6 gives a reproduction of Zanstra's curves $f(x)$ versus X for the range of $x=1$ to 10^{-6}. A plot of $1/i$ versus $f(x)$ for different values of X should, by eq 1, give a straight line for which the intercept on the $1/i$ axis is the reciprocal of the saturation current, I. It should be noted that the constants in eq 1 and the approximations in the theory do not directly influence the value of $1/i$ but serve to rectify the curvature which would otherwise appear in a simple plot of $1/i$ versus $1/X$.

The validity of the Jaffe-Zanstra theory was tested in the present work by measuring a fixed 300-kv X-ray beam at pressures of 1.0, 6.80 and 10.13 atm, respectively. In the ionization chamber, a plate separation of 30 cm was used, so that no wall correction was necessary at any pressure. Figure 7 shows the current-voltage curves at 1 and 10.13 atm (coordinate scales at right and top) and the $1/i$ versus $f(x)$ (scales at left and bottom) for 10.13 atm. The intercept of this $1/i$ plot and a similar plot at 6.8 atm gave the following values of I after correction for air absorption: I (10.13 atm)/10.13=1.076; I (6.8 atm)/6.8=1.078; and I (1 atm)=1.078. The agreement is better than the

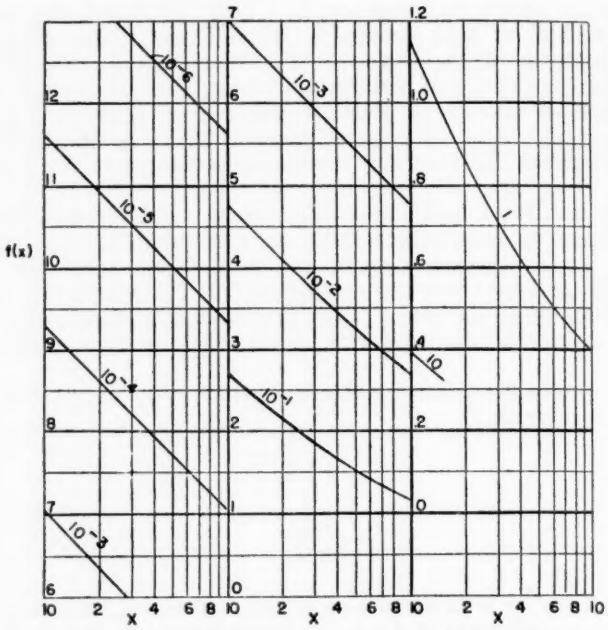

FIGURE 6.—*Zanstra's curves for evaluation of* $f(x)$.

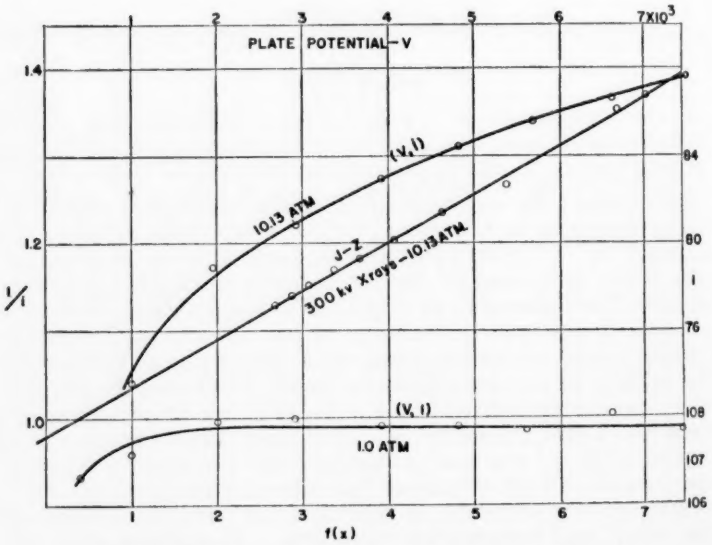

FIGURE 7.—*Normal saturation and J–Z plots at 10 atm.*

experimental error of about ±0.5 percent in the particular measurements warrants. These measurements were made with a maximum of 8,000 volts on the plate (field strength=27 v/cm·atm).

It was, of course, necessary to see if the measurements made at field strengths between 3.3 and 27 v/cm· atm formed an adequate basis for extrapolation or if higher fields were required. Figure 8 shows the $1/i$ versus $f(x)$ curve obtained from the data plotted in figure 5. Here it is evident that it is not necessary to exceed the field of 270 v/cm at 10 atm or 27 v/cm·atm, although by going to fields as high as 67 v/cm·atm the extrapolation is somewhat shortened. Under the particular conditions at 27 v/cm·atm the current is 87 percent of the saturation current, I, and at 67 v/cm·atm it is 94 percent.

The extrapolation, therefore, amounts here to about 6 percent of the total length, as compared with values as large as 45 percent for

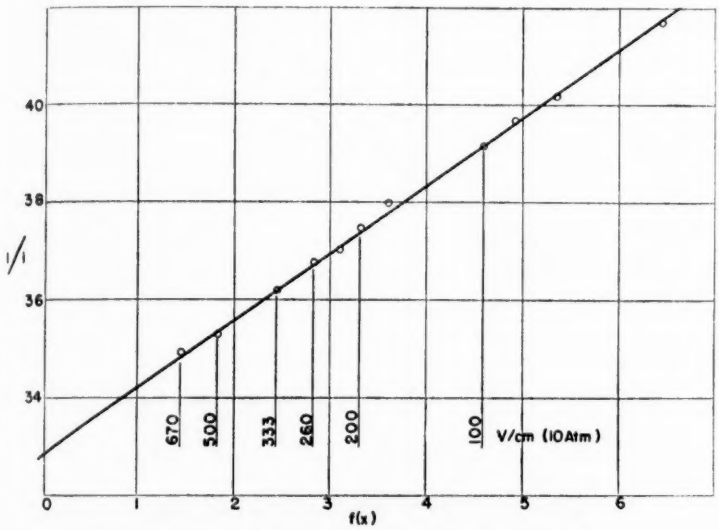

FIGURE 8.—*J–Z plot for field strengths up to 670 v/cm.*

higher pressures and the higher fields used by Clay [10 to 12] and Broxon and Meredith [4]. (Reduced to atmospheric pressure, their field strengths were usually much smaller than ours.) By decreasing the plate separation to 18 and 7 cm, the maximum field strength was increased to 45 and 80 v/cm·atm, respectively, and the maximum measured current was 96 and 97 percent, respectively, of the saturation value obtained by the *J–Z* extrapolation.

The chamber was not usable for our purposes under these conditions, since the decreased plate separations would introduce undesirable wall effects. The results indicated, however, that the *J-Z* plot would be linear to within at least 3 percent of the saturation current value and hence the extrapolation used with the wider plate separations is similarly justifiable.

For convenience it is frequently desirable to make comparative measurements without, for each condition, going through the entire *J-Z* extrapolation procedure. Such a procedure is permissible under conditions (1) where the ionization density does not vary over too wide limits, or (2) where measurements are well inside the region

where the *J-Z* curve is linear and the field strengths do not differ too greatly, or (3) both.

A check of the first point was afforded in testing the validity of the inverse-square-law plot of figure 4. The points on this plot were obtained at a fixed field strength of about 26v/cm·atm, giving a value for $f(x)$ of about 3. To check their validity, complete *J-Z* extrapolations (fig. 9) were made for two distances between the radium and the exit face of the diaphragm, such that the edge correction for the diaphragm should be practically negligible between the two positions. From the *J-Z* computations the saturation value for 61.0 cm is 0.0273

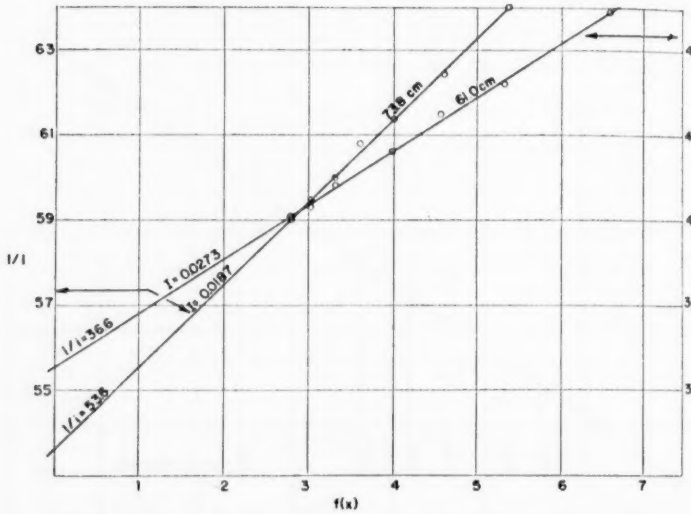

FIGURE 9.—*J-Z plots for different radium-diaphragm distances.*

and for 73.8 cm is 0.01865. The ratio 0.0273/0.01865=1.464 should, if the theory is applicable, be that of the ionization produced in the two cases, which in turn should be inversely proportional to the squares of the distance. This latter ratio is $(73.8/61.1)^2=1.458$, and agrees with the ratios of the ionization to 0.4 percent, which is within the experimental error. It is clear from the plotted points (fig. 9) that even with the poorest choice of the position of the intercept the saturation value could not be in error by as much as 0.5 percent.

The second point is illustrated by the curves in figure 10, where two *J-Z* curves are drawn through points measured for the same beam (hence, same ionization density) but with different plate separations and hence, different field strengths. The resultant straight lines converge slightly, so that the ratio of the two ordinates for any single value of $f(x)$ over the range of $f(x)$ shown has the constant value 1.023. Similar ratios at a given applied voltage are very nearly 1.00. This divergence arises from the difference in field strengths and will be discussed later.

It should be pointed out that Zanstra's evaluation of Jaffe's equation fails for low field strengths, so that the *J-Z* plot is no longer linear, the points falling above the extended straight line. The point

at which this deviation begins is variable and depends upon the nature of the gas, pressure, ion density, and field strength. Under the conditions of this study, the deviation begins for fields below about 2 vicm·atm or values of $f(x)>7$. The effect has been described by Clay and van Kleef as the condition where volume recombination begins to become relatively dominant in comparison with the columnar recombination.

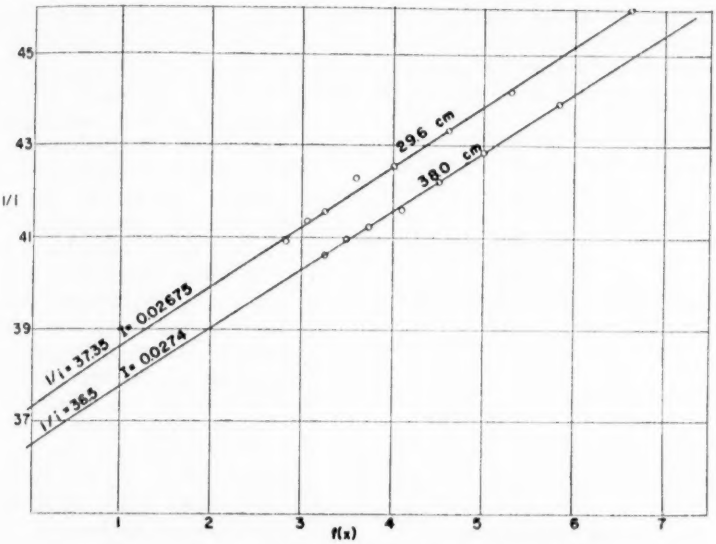

FIGURE 10.—*J-Z plots for different plate separations.*

V. EFFECT OF PLATE SEPARATION

In their gamma-ray measurements with a large open-air guarded-field ionization chamber, Kaye and Binks [13] found a plate separation of about 3.0 m apparently sufficient to prevent the impingement of an appreciable amount of secondary radiation upon the plates. On this basis we have done much of our exploratory work with a separation of 30 cm at a pressure of 10 atm, which is equivalent to Kaye's spacing.

However, to be certain that the chamber was free from wall effects, ionization currents were measured for different plate separations. For these, the beam width was about 2 cm at the center of the chamber. Curve *A* in figure 11 was obtained by simply increasing the plate spacing while keeping a fixed potential of 7,000 volts between plates. Saturation was apparently reached at about 30 cm. However, with increasing distance between the plates, there is a proportionate decrease in field strength; consequently, the flattening of the curve, *A*, may be caused in part by the decrease in field strength. To eliminate this factor, the second curve, *B*, was obtained with the same field strength at all plate spacings. In this latter case, field saturation was not definitely reached below about 35 cm, which spacing, or one greater, was used in the final radiation measurements. These studies have shown the unreliability of comparing ionization

measurements made under different field strengths. Above about 2.00 v/cm·atm, comparisons at the same field strength are valid, provided the radiation intensities and qualities are about the same.

The results of curve *B* in figure 11 were checked by means of the *J-Z* extrapolation made at plate spacings of 29.6 and 38.0 cm and shown in figure 10. The ratio $I_{38}/I_{29.6}=0.02740/0.02675$ is 1.023 as compared with a ratio $i_{38}/i_{29.6}=26.8/26.3$ which is 1.019 (from figure 11) for the curves made at constant field strength.

Comparing these results with the work of others, a fairly good agreement is found with Kaye and Binks [13]. We find an ionization increase of only about 2 percent by increasing our plate spacing from effectively 3 to 3.5 m (30 to 35 cm at 10 atm), beyond which the change is not measurable. Failla and Marinelli [14] have shown the deficiency of the free-air chamber used for gamma-ray measurements by Failla and Henshaw [15]. The plate spacing of 1 m at atmospheric pressure used in their earlier work was insufficient. Mayneord's [16] plate spacing of 30 cm at 1 atm was clearly too small, as he subsequently pointed out.

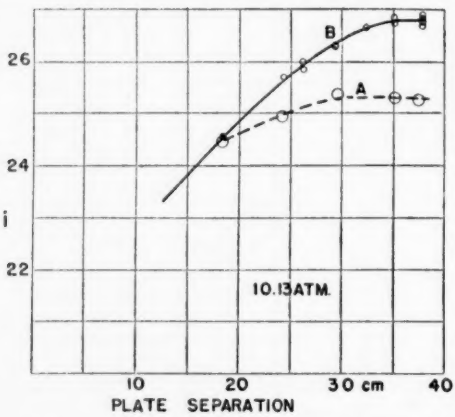

FIGURE 11.—*Plate separation curves at 10.13 atm.*

Two previous studies of gamma-ray measurement have been made with high-pressure ionization chambers. Clay and van Kleef [17] used an argon-filled chamber with metal-grid electrodes 5 mm apart, at fields from 100 to 4,000 v/cm at 100-atm pressure. (This was equivalent to 40 v/cm·atm). Clay and van Tijn [18] obtained with this chamber, by means of the *J–Z* extrapolation, a value for Eve's constant which is in reasonable agreement with other determinations. However, since their plates had an effective separation of only about 50 cm at 1 atm, wall effects played some part in their result.

Friedrich, Schulze, and Henschke [19] used air at pressures up to 139 atm in a graphite chamber having an electrode separation of what appears to be 8 mm in their drawing; but they took no account of columnar ionization. Their effective plate separation at 1 atm was on this basis about 110 cm, hence the measurements also involve wall effect.

VI. ELECTRONIC EQUILIBRIUM

To insure the accurate evaluation, in roentgens, of gamma rays, using a free-air chamber, it is necessary to have what is known as a state of electronic equilibrium over the region from which the ions are measured. This condition is realized when the electrons which escape from the measuring volume are exactly compensated for by electrons which enter it from the outside space. Applied to the

measurement of gamma radiation from radium by the free-air ionization chamber, this requires that the volume from which the ions are measured be surrounded by an envelope of air having a thickness in all directions at least equal to the maximum range of the secondary electrons in those directions.

Where a narrow collimated beam of radiation is involved, this requires that between any limiting diaphragm or filter and the ionization chamber, there must be a free-air path of a length at least equal to the longest paths of any scattered or recoil electrons. Since the secondary electrons involved in gamma-ray scattering are predominantly in the forward direction, a very considerable distance between the lead diaphragm, dd', and the collector electrodes of the ionization chamber is required. Kaye and Binks [13] found that at atmospheric pressure a distance of 7 m was apparently sufficient, whereas Friedrich's measurements [19] indicated about 15. Using our equipment at 10 atm,

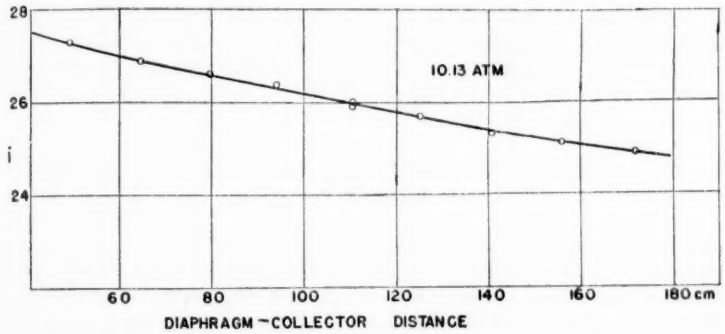

FIGURE 12.—*Air absorption of gamma rays at 10 atm.*

it was possible to test this over a range equivalent to 6 to 21 m at atmospheric pressure.

Following our earlier procedures [1], ionization measurements were made for distances between the collector and the window over the above range. Inasmuch as the diaphragm was but 10 cm outside the aluminum window of the pressure tank, distances from the aluminum window to the collector were used. Figure 12 shows the results of these measurements. It is seen that the decrease in ionization is linear within less than 0.5 percent over the range of 70 to 150 cm, which is equivalent to a range of 7 to 15 m at 1 atm. The small increase, above 150 cm and below 70 cm, may be ascribed to scattering from the ends of the pressure cylinder. All measurements given in this paper were made at distances equivalent to 9 m at 1 atm unless otherwise noted.

It is clearly evident from the measurements in figure 12 that a state of electronic equilibrium existed in the forward direction. From plate-separation measurements of figure 11, curve B, a similar state in the lateral direction is assured. However, a further check on these conclusions was obtained in trying to find Failla's "cloud effect" [14]. Two sets of measurements were made at distances, L, between the collector and the window of 58.9 and 120.1 cm, wherein the satura-

tion currents were determined by the *J-Z* method. The ratio of the corresponding values of I was 1.023, as compared with a ratio of 1.027 derived from figure 12 for the air absorption alone.

These measurements show the existence of electronic equilibrium within experimental errors but does not provide a fair test for the cloud effect. Since our minimum distance to the limiting diaphragm was about 6 m, we may have been outside the region where any expansion of the cloud could be detected. Also, our collector having an effective length of 2.5 m at 1 atm, any *small* change in the effect of the cloud shape would be masked. Any attempt to verify the effect at lower pressure would have been unreliable, because then a state of lateral electronic equilibrium would no longer exist.

As indicated, the data in figure 12 may be used to determine the air absorption for the radiation used. The absorption, which is found to be 7.7 percent per meter at 10 atm, requires that a correction be applied to all absolute measurements or all comparative measurements wherein L is changed; as for example, the inverse-square-law measurements shown in figure 4. The above value reduced to 1 atm gives an absorption of 0.77 percent per meter, in good agreement with the lower figure of 0.75 calculated from Kaye and Binks' work [13].

VII. THE MEASUREMENT OF GAMMA RADIATION IN ROENTGENS

The magnitude of gamma radiation in roentgens has been variously defined in terms of the quantity of radium, time, filtration, and distance. In many cases, the literature has not been clear with regard to the various corrections applied in making the measurement, and this has resulted in confusion in the final results. We shall, therefore, risking repetition, describe in detail the various measurements and corrections employed in this study.

For reference purposes, the "emission constant," Q_0 of radium is defined as the number of roentgens measured in 1 second at 1 cm from 1 g of radium, assuming the complete exclusion of any beta rays. This implies that the radium salt must be enclosed in a filtering container of known gamma-ray absorption or by an air envelope of equivalent thickness.

In the radiological field, however, the quantity of gamma radiation, Q, from radium is expressed as equal to the number of roentgens per hour produced by each milligram of radium, acting through 0.5 mm of platinum, at a distance of 1 cm from the radium. Since the radiation varies inversely as the square of the distance, the gamma radiation is then

$$Q=r/D^2mT,$$

where r is the number of roentgens at a distance of D centimeters from m milligrams of radium, in T hours. Here, the quantity of radium is taken as the actual mass of radium B and C in equilibrium with their disintegration products. The 0.5-mm platinum filtration is added for the principal purpose of eliminating any beta radiation, and enters the experiment as a purely arbitrary factor for which no absorption correction is made. (Should correction be made for the absorption of the gamma radiation in the platinum, the quantity

result would be several percent larger, and not expressed consistently with the radiological definition.)

The radium employed in this study was of the order of 500 mg contained in a platinum cylinder 4.45 mm long and 9.95 mm outside diameter, having walls 0.500 mm thick. It was necessary to know the actual radium content for the proper evaluation of our results. The method of calibration is that uniformly used in the national laboratories of the various countries and has been recently described by Perry [23].

Our radium was calibrated in the National Bureau of Standards radium laboratory under the supervision of L. F. Curtiss. The usual substitution method was employed, and he states that the measurements are believed to be accurate within 0.1 percent. The electroscope was encased in a thick lead shield and, hence, differed markedly from our free-air ionization chamber. The comparison was made against a number of individually calibrated radium preparations contained in thin-glass tubes and bunched together so as to approach as nearly as possible the geometrical configuration of the preparation under calibration. By this means the absorption of radiation in the salt of the unknown and the comparison sources was made as nearly the same as possible and, therefore, balanced out. To test for this, the comparison tubes were arranged in a variety of reasonable configurations, and it was found that any calibration differences were negligible. The final result would not, of course, give the actual number of milligrams in the unknown, since the radiation from the latter was filtered by the additional 0.5 mm of platinum, while that from the standard was measured after passing through the glass only.

The Bureau's certificate stated that the sample had a gamma radiation equivalent to that from 466.6 mg of radium.[4] Correction must be made, however, for the absorption of the emitted radiation in the salt itself (radium sulfate), because the amount of radiation finally emerging varies with the configuration of the salt. An absorption coefficient applicable to this problem was very kindly supplied to us by G. C. Laurence.[5] He gives a value of 0.037 cm^2/g, which he determined under experimental conditions comparable to ours. For making this test, he placed the radium salt in a funnel-shaped thin-walled tube. In one measurement the radium was spread thinly over a considerable area normal to the direction of measurement, and hence offered a negligible absorption of the radiation in the salt. In the second measurement, the container was inverted, so that the salt was packed in a long thin stem such that in its lengthwise direction a considerable absorption of the radiation took place. The absorption coefficient was then derived from the difference between the two measured radiations.[6]

Assuming that, on the average, all the radiation is absorbed by only half of the radium content, an absorption value of 1.47 percent is derived. This is in agreement with an integrated value, since it must

[4] Had the radium been contained in a thin-glass tube (as is used for the standards) its gamma radiation would have been 4.3 percent greater than the certified value. (Under the conditions of calibration with a lead-walled electroscope, the platinum absorbed 4.3 percent of the radiation.) Therefore, the *actual radium-element content* of the preparation here used was 486.6 mg.

[5] National Research Council of Canada. Personal communication.

[6] Laurence points out that absorption of the gamma rays in the source itself is complicated by the fact that we are dealing with the net absorption, which is a difference between the true total absorption and scattered radiation. The net-absorption coefficient will be considerably lower than the more usually quoted coefficients, which are total true absorption. Since the net absorption is so small, the effect on the absorption coefficient of any change in radiation quality is negligible.

be assumed that there is no change in the quality of the radiation in traversing the salt—a not unreasonable assumption since the total absorption is so small.

Another absorption figure was supplied to us by Dr. G. W. C. Kaye.[7] For a cylinder of approximately the same diameter as ours but with 2.5 mm inside length, he has determined a correction of 1.6 percent, which for our conditions would amount to nearly 3 percent—a figure higher than any of those computed above. His work is expected to be published at an early date.

In the final calculations a correction of 1.47 percent for absorption in the salt has been applied to the radiation from 486.6 mg *actual* content of our capsule. We thus deal with an *effective radium content of 479.4 mg* in the final result.

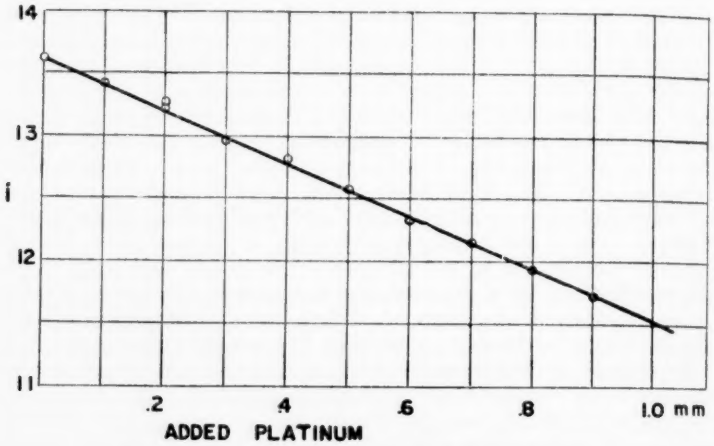

FIGURE 13.—*Platinum absorption of gamma rays.*

Although not very great, the correction for the absorption of the gamma radiation in the radium salt probably represents the largest uncertainty in our experimental results.

It should be emphasized that the 4.3-percent platinum-absorption correction in the original radium calibration applies only to the particular measurement technique employed by the radium laboratory. To make possible correction of our results to other platinum filtrations, separate platinum-absorption measurements were made using the measurement technique described in previous sections. Successive layers of 0.10-mm platinum foil were cemented lightly to the face of the capsule and ionization readings made with the back of the capsule always in the same position within the collimating tube (figure 2). The results, shown in figure 13, indicate uniform absorption over the range of 1 mm of added platinum. The linearity of the absorption curve would, therefore, indicate that under our conditions of measurement, the 0.5-mm platinum wall absorbs approxi-

[7] National Physical Laboratory. Personal communication.

mately 7.2 percent of the gamma radiation. This figure does not enter our calculations of Q, since the filtration by 0.5 mm of platinum is included in the definition, but does enter in the evaluation of the emission constant, Q_0.

To obtain an estimate of the precision of the measurement, the errors in the several quantities involved in the determination of the emission constant of radium and the degree to which they enter the final results are listed in table 2.

TABLE 2.—*Errors involved in the measurement of gamma rays*

Quantity	Residual error	Error in result
Group A:	*Percent*	*Percent*
Radium calibration	±0.1	±0.1
Salt absorption	20	.4
Group B:		
Air absorption	3	.2
Diaphragm edge	10	.2
Distance of radium	0.2	----------
Current measurement	.3	.3
Saturation current	.3	.3
Volume measurement	.2	.2
Pressure	.3	.3
Average deviation from mean in all observations	.5	----------

The errors fall into two groups: A, those involved in determining the effective quantity of radium; and B, those involved in measuring the gamma radiation by our set-up.

In group A the calibration of the radium is accepted with the estimated possible error. Likewise, the residual error in the absorption by the salt lies in the uncertainty of Laurence's absorption coefficient.[8]

In group B, also, the residual errors in each measurement are as indicated. The average deviation from the mean in all observations did not exceed 0.5 percent. The possible error in distance of the radium enters, because this is measured to the center of the capsule, whereas it might be argued that the distance should be measured to some other point. The residual error in deriving the saturation current is obtained from the greatest possible spread in the value of $1/I$ for $f(x)=0$ due to the choice of the straight line drawn through the plotted points.

The accuracy of measurement obtained by the square root of the sums of the squares of the individual errors in group B alone is ± 0.25 percent and for both groups, A and B together, ± 0.28 percent. Since the sum of the errors in group A is 0.41 percent, it is seen that the effect of the errors of measurement in the present work on the final result is negligible in comparison with the effect of the uncertainty in the quantity of radium and loss by self-absorption.

In table 3 are given the various experimental values and apparatus constants involved in the measurement of gamma rays in roentgens.

[8] Since a question of interpretation is involved in this correction, there is a possibility of as much as a 2-percent error in the final result, depending upon the particular coefficient used. The use of any other probable coefficients will tend to increase the final value of the emission constant.

TABLE 3.—*Factors in the calculations of the emission constant*

Capacitance (C)	851 $\mu\mu$f
Compensating volts/sec (V/t)	1.791×10^{-4} (extrapolated value)
Distance (D)	62.0 cm
Pressure (P)	9.67 atm
Temperature (T)	302° K
Measuring volume (W)	19.60 cm³
Platinum absorption factor (k_p)	1.072
Effective radium content (R_e)	479.4 mg
Air-absorption factor (k_a)	1.081
Slit edge-correction factor (k_s)	0.980

The following equation will give the emission constant, Q_0, for radium B and C after allowing 7.2 percent for the absorption of the radiation in platinum:

$$Q_0=\frac{0.9\times CV\times T\times D^2\times k_p k_a k_s}{300\times W\times t\times 273\times R_e\times P} \tag{5}$$

$$=2.43\pm0.01 r/g\cdot\text{sec at 1 cm.}$$

In terms of the radiological unit the emission is

$$Q=8.16\pm0.04 \text{ r/mg}\cdot\text{hr at 1 cm.}$$

Various summaries have been made of the experimental values obtained for Q using thimble and other chambers, which, for comparison with our results, we give in table 4. In this table, column 3 gives the number of separate previous determinations of Q, which are averaged in column 4. Column 5 gives the maximum divergence between the averaged values. Column 6 gives the new value presented by each author.

TABLE 4.—*Summary of thimble chamber measurements*

Summary by—	Reference	Number of determinations	Average value, Q	Spread	Author's own value
				Percent	
Mayneord (1934)	[20]	5	8.6	13	8.3
Kaye and Binks (1938)	[13]	9	8.0	17	[a] 8.0
Friedrich (1938)	[19]	9	8.15	26	7.8
Rovner (1938)	[21]	12	8.55	15	.....
Laurence (1938)	[22]	6	8.35	9	.....

[a] Free-air chamber as well as thimble chamber.

It is interesting to note that while the above summaries are based on essentially the same experimental sources, they vary over a range of some 7 percent. This is because the different workers, in preparing the summaries, have had to correct the final results of the other workers for filtration or salt absorption and have used, for the purpose, differing correction factors. Other observers have weighted

their summaries by discarding results which for one reason or another seemed questionable to them. This is, of course, a perfectly valid procedure, but it does show that the most probable value of Q is not to be had by a simple averaging of the various final results obtained in many different laboratories.

Our own value of Q=8.16 r/mg·hr at 1 cm is about 2 percent higher than the only other value obtained under free-air conditions—8.0 r/mg.hr at 1 cm by Kaye and Binks. However, if we had used their value for the salt absorption, our result would have been still higher by about 1½ percent, and hence the disparity even greater.

Our own final values of Q_0 and Q are presented with reservations as to the accuracy of the radium-salt absorption correction, and further corrections may be made in the future. Further studies by experts in the radium field may yield a more accurate evaluation of this absorption coefficient.

VIII. CONCLUSION

The primary purpose of this investigation has been to investigate the possibilities of measuring the very short wavelength radiation by means of a pressure ionization chamber. The results with gamma rays show that such wavelengths may be satisfactorily measured in roentgens so long as the pressure is sufficient to give an effective free path between the beam and measuring electrodes equal to the longest range of the recoil electrons. Since the ranges overlap those involved in X-ray scattering up to 1.5 MV, it may be concluded that X-rays up to at least 1.5 MV may be measured in roentgens under free-air conditions. It is, therefore, possible to directly calibrate thimble chambers against a free-air standard for all excitations presently available, and thus provide a logical extension of the useful range of thimble chambers. Likewise, having once established a value for r/mg·hr at 1 cm, it is possible to effect a direct calibration of radioactive preparations in terms of roentgens without further reference to the primary radium-salt standards.

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SECOND IONIZATION CONSTANT AND RELATED THERMODYNAMIC QUANTITIES FOR MALONIC ACID FROM 0° TO 60°C[1]

By Walter J. Hamer, John O. Burton,* and S. F. Acree

ABSTRACT

The second ionization constant of malonic acid in aqueous solution was determined at 0° to 60° C from measurements of the electromotive force of galvanic cells without liquid junction. Solutions containing sodium acid malonate, sodium malonate, and sodium chloride were employed for these determinations. From the values of the ionization constants, the closest distance of approach, or the so-called diameters, of the ions in the solution was calculated for the different temperatures. These ionic diameters, the electromotive force, and the known molalities were then employed to calculate pH values of the solutions. The ionization constant at the different temperatures was determined from the experimental data by three different methods, using a least-square calculation in each. The values are different for the various temperatures, and may be computed for temperatures from 0° to 60° C, inclusive, by the equation

$$\log K_2 = -\frac{1053.08}{T} + 20.3223 \log T - 0.05838\ T + 0.0000236\ T^2 - 37.1402.$$

Equations were formulated to express the variation of pH as a function of the ionic strength of the solution, to give the heat of ionization of the acid malonate ion, and to give the difference in the specific heats of the ions and the undissociated acid malonate ion at each temperature. The change in free energy and entropy for the ionization of the acid malonate ion were also calculated for each temperature. All of these quantities are of importance in arriving at explanations for the variation of hydrogen-ion activity with temperature.

It has been found that solutions containing equal concentrations of sodium acid malonate, sodium malonate, and sodium chloride, each varying from 0.001 to 0.044 molal, have pH values ranging from 5.272 to 5.761 at 0° to 60° C. These solutions are suitable for use as pH standards.

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[1] This paper includes data presented in a dissertation submitted by John O. Burton to the Faculty of the Graduate School of the University of Maryland, represented by M. M. Haring, of the Department of Chemistry, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June 1937.

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I. INTRODUCTION

Solutions of most dibasic acids and their salts resist a change in hydrogen-ion activity on dilution or on the addition of a small amount of acid or alkali. This ability to resist a change in hydrogen-ion activity is called buffer capacity. Hence, such solutions are called buffer solutions, and they are well suited for use as solutions of a definite and known hydrogen-ion activity, or as pH standards. Only qualitative data are available on the buffer capacity, the pH values, and the thermodynamics of solutions of malonic acid and its salts, especially for a wide range of temperature. These quantities are expressed in terms of the equilibrium values for the dissociation of malonic acid. The equilibria for the two steps in the dissociation of malonic acid into its ions are represented by definite numerical quantities, called ionization constants. It is the purpose of this report to present (a) quantitative data for determinations of the second ionization constant of malonic acid, (b) pH values for some solutions of malonate salts, and (c) related thermodynamic data.

In previous reports [1, 2][2] "apparent"[3] values of the first and second ionization constants for malonic acid at 25° C were given. These values were termed "apparent" in that only partial corrections were made for the presence of salts in the solutions which were employed for their determinations. Furthermore, these values were obtained from measurements of galvanic cells with liquid junctions. The values of the potentials of liquid junctions can only be estimated and cannot be obtained on a thermodynamic basis [3]. Hence, the values reported previously also included uncertainties arising from liquid-junction potentials. In order to determine the real or thermodynamic values of the constants and eliminate the uncertainties due to liquid junctions, measurements were made of the hydrogen-ion activities of solutions of malonate salts of different known molalities by means of galvanic cells without liquid junctions, as described in a previous Research Paper [4].

This paper will be confined to determinations of the second constant and related quantities. Values [1, 2, 5] previously reported in the literature for this constant are for temperatures of 18° and 25° C only. In practice, dibasic acids and materials containing them are frequently studied or used at other temperatures. It is, therefore, important that a knowledge of the equilibrium values for their dissociation at various temperatures be made available. With this in view, measurements were made at 5° intervals from 0° to 60° C. From measurements of the effect of temperature upon the equilibrium value, it is possible to determine the increase in the free energy, entropy, and the heat of ionization for the ionic dissociation. These thermodynamic quantities are of importance in general studies of ionic dissociation, of the effect of temperature on the hydrogen-ion activity of solutions, and for additional information about the properties and structure of organic materials in aqueous solutions.

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[2] Figures in brackets indicate the literature references at the end of this paper.

[3] The term "apparent" has also been used to designate the ionization constants of indicators and other tautomers. The ionization constant of an indicator is a complex one, involving both the ratios of the tautomeric molecules or ions and their separate ionization constants, and is, therefore, termed "apparent." See Acree, Am. Chem. J. **38**, 1 (1907); White and Acree, J. Am. Chem. Soc. **40**, 1092 (1918); and Birge and Acree, J. Am. Chem. Soc. **41**, 1031 (1919). The use here of the term "apparent" should be distinguished from its use in reference to tautomeric indicators.

II. DISSOCIATION OF MALONIC ACID

Malonic acid, $H_4C_3O_4$, dissociates in aqueous solutions in two steps represented by the equations

$$H_2An \rightleftharpoons H^+ + HAn^- \quad (1)$$

and

$$HAn^- \rightleftharpoons H^+ + An^=, \quad (2)$$

where H_2An, H^+, HAn^-, and $An^=$ are employed to denote malonic acid, hydrogen ion, acid malonate ion, and malonate ion, respectively. This paper is confined to the determination of the equilibrium value for the second step in the ionization of malonic acid, and therefore, only eq 2 need be considered here. The ions represented in eq 2 exist in solution in dynamic equilibrium, which is expressed by the law of mass action [6] given by the equation

$$K_2 = \frac{a_H a_{An}}{a_{HAn}} = \frac{m_H m_{An} \gamma_H \gamma_{An}}{m_{HAn} \gamma_{HAn}}, \quad (3)$$

in which a, m, and γ represent, respectively, the activity; the concentration of the solution in moles per 1,000 g of water, or molality; and the activity coefficient of the species denoted by subscripts; and K_2 represents a definite numerical value for the equilibrium at a given temperature and pressure, and is conventionally termed the second ionization constant.[4]

For determinations of K_2, solutions are prepared which contain only the ions of malonic acid represented in eq 3, and measurements are made of the hydrogen-ion activity of these solutions. It was shown in a previous paper [1] that an aqueous solution containing one-third or more of a mole of sodium malonate to 1 mole of sodium acid malonate will satisfy this requirement. It may be shown from known facts about the hydrolysis of these salts and the ionic equilibria that besides the Na^+ ions, only H^+, HAn^-, and $An^=$ ions will be present in such solutions in significant and measurable amounts. For convenience in subsequent calculations of K_2, solutions were prepared containing equal molal quantities of sodium acid malonate (m_1) and sodium malonate (m_2). Complete dissociation of these salts[5] is assumed, and hence they may be considered to ionize according to the equations

$$Na_2An \rightarrow 2Na^+ + An^= \quad (4)$$

$$NaHAn \rightarrow Na^+ + HAn^-. \quad (5)$$

Therefore, upon substitution,

$$K_2 = \frac{m_H m_2 \gamma_H \gamma_{An}}{m_1 \gamma_{HAn}}. \quad (6)$$

[4] If the ions in solution conformed to the law for ideal solutes, only the molalities would be used to define K_2. Actually, they do not; therefore, the activity coefficients are introduced to express their deviations from the laws of ideal solutes. The values of the activity coefficients are unity at infinite dilution, at which point the ions are considered to behave as ideal solutes. See Falkenhagen, Electrolytes, p. 6 [translation by Bell] (Clarendon Press, Oxford, London, 1934) for conceptions of infinite dilution.

[5] Salts of the alkaline metals are considered by most workers to be completely dissociated at all concentrations of the salt solutions. Ample justification of this assumption has been reported in the literature from results obtained from experiment and conclusions deduced from theory. See Falkenhagen, Electrolytes, p. 51 [translation by Bell] (Clarendon Press, Oxford, London, 1934); Glasstone, The Electrochemistry of Solutions, p. 134–162 (D. Van Nostrand Co., Inc., New York, N. Y., 1937); Lewis and Randall, Thermodynamics, p. 317 (McGraw-Hill Book Co., Inc., New York, N. Y., 1923).

However, the HAn^-ion partially ionizes further in accordance with eq 2, or

$$HAn^- \text{ or } [m_1 - m_H] \rightleftharpoons H^+ \text{ or } [m_H] + An^= \text{ or } [m_H] \tag{7}$$

to give an additional amount of $An^=$ion equal to the hydrogen-ion concentration. Therefore, the actual molality of the HAn^- and $An^=$ ions in solution is not equal to the stoichiometrical molalities of the salts, but equal, respectively, to $[m_1 - m_H]$ and $[m_2 + m_H]$. Hence

$$K_2 = \frac{[m_H][m_2 + m_H]\gamma_H\gamma_{An}}{[m_1 - m_H]\gamma_{HAn}}. \tag{8}$$

By measuring the hydrogen-ion activity of the solution and using the known values of m_1 and m_2, values of $K_2\gamma_{HAn}/\gamma_H\gamma_{An}$ may be obtained for a series of values of $[m_H]$ $[m_2 + m_H]/[m_1 - m_H]$. To obtain K_2, values of $K_2\gamma_{HAn}/\gamma_H\gamma_{An}$ are plotted against the ionic strengths of the solutions, μ, defined as half the sum of the molality of each ion multiplied by the square of its valence. Extrapolation is then made to infinite dilution, or zero ionic strength, at which point $\gamma_{HAn}/\gamma_H\gamma_{An}$ is equal to unity (see footnote 4).

Two other reactions occur between the ions in solution, both of which are insignificant in comparison with the experimental error. The ions of the dibasic salt hydrolyze according to the reaction

$$An^= + H_2O \rightarrow HAn^- + OH^-, \tag{9}$$

and an amount of malonic acid is formed in the reaction

$$2HAn^- \rightarrow H_2An + An^=. \tag{10}$$

If X is the molality of OH^-ion formed in reaction 9, and Y is the molality of H_2An formed by reaction 10, and these reactions are assumed to occur independently, values of X and Y may be obtained by the mass action expressions for these reactions, or by

$$\frac{[X][HAn^- - H^+ + X]}{[An^= + H^+ - X]} = K_h = \frac{K_w}{K_2} \tag{11}$$

and

$$\frac{[Y][An^= + H^+ + Y]}{[HAn^- - H^+ - Y]^2} = \frac{K_2}{K_1}, \tag{12}$$

in which K_h denotes the hydrolysis constant, K_w the ionization constant of water, and K_1 the first ionization constant of malonic acid. Using 0.0009867 M (the lowest molality employed in this investigation, and for which the effect of the above reactions would be greatest) for the molalities of HAn^- and $An^=$; 1.67×10^{-3} for K_1 [2]; 2.104×10^{-6} (table 6) for K_2; and 1.008×10^{-14} for K_w [7] in the equations, X and Y are found to be 4.5×10^{-9} M and 1.23×10^{-6} M, respectively, at 25° C. These amounts are so small that reactions 9 and 10 may be disregarded, and eq 8 may therefore be used for calculations of accurate values of K_2. Simultaneous occurrence of these reactions in solution, which is the case, would give even smaller values of X and Y.

III. EXPERIMENTAL

1. MATERIALS

Malonic acid obtained from the Eastman Kodak Co. was used for the preparation of the solutions. Its purity (98.92 percent) was determined by titration with a standardized solution of carbonate-free sodium hydroxide, using phenolphthalein as the indicator. This method (neutralization equivalent) of ascertaining the purity, although subject to the usual errors of titration, is the best one available. The melting point, when measured in the usual manner, is not sufficiently well defined to be used as a reliable test of purity [8], and the other accepted methods for the determination of molecular weights are not well adapted to malonic acid.

The malonic acid was purified as follows. It was triturated, washed six times with redistilled carbon tetrachloride to remove esters, and dried at 60° C. (higher temperatures cause decomposition) for 48 hours. It was then extracted with diethyl ether (previously dried over metallic sodium and redistilled) in a Soxhlet extractor, and then dried under reduced pressure at 60° C for 96 hours to remove the ether. It was finally rewashed with redistilled carbon tetrachloride and dried at 60° C for 96 hours. The purity of the acid was found by titration to be 99.88 percent by weight. A second and third repurification removed no more impurities. A small portion of the purified acid was then extracted and recrystallized from a mixture of benzene and ether containing 5 percent of petroleum ether, recommended as a solvent for purification of malonic acid by Vogel [9]. No more impurities were removed by this solvent. The purity of the malonic acid used in this work was 99.84 to 99.92 percent by weight, based on an estimated error of 0.04 percent in titration. The ash content determined by ignition of a portion to a dull red heat in a platinum crucible was 0.005 to 0.007 percent. In the preparation of the solutions, allowance was made for the percentage of inert impurities, which were considered to be due to the occlusion of the solvent used in the purification.

The sodium hydroxide solution was prepared from high-grade material which exceeded the ACS specifications for analytical reagents.[6] It was freed of carbonate by preparing a saturated solution, siphoning off the supernatant liquid above the insoluble sodium carbonate into a bottle, and diluting to 0.5 *N* with deaerated conductivity water. In all manipulations with sodium hydroxide solutions, the apparatus was protected from the atmosphere by soda-lime tubes, or by passing a stream of CO_2-free air over the apparatus or solutions. The solution was standardized against benzoic acid, National Bureau of Standards Sample 39e, using phenolphthalein solution as the indicator. Results of four titrations agreed to 0.02 percent.

The hydrochloric acid solution was prepared by the method of Brunel and Acree [10]. Hydrogen chloride gas formed in a Kipp generator by the action of concentrated sulfuric acid on ammonium

[6] Analysis was made by the Chemistry Division of this Bureau.

chloride was passed into conductivity water. After leaving the generator, the gas was passed at a rate of two bubbles per second through a wash bottle containing concentrated sulfuric acid. The hydrochloric acid was tested and found free of sulfate. The concentration of the acid was determined in two ways. One was by weighing the flask containing a known weight of conductivity water before and after the introduction of the gas, and subsequent calculation of the molality. The other was by weight titration with the standardized sodium hydroxide solution, using phenolphthalein as the indicator. The two analyses agreed to 0.04 percent.

2. SOLUTIONS

The solutions employed in this investigation were prepared from a stock solution, containing equal molal quantities (0.09923 *M*) of sodium malonate, sodium acid malonate, and sodium chloride, by dilution with known weights of conductivity water freed of dissolved air and carbon dioxide. The specific conductance of the water was 1.0×10^{-6} mho. The presence of chloride ion in the solutions is required for the emf method without liquid junctions (section IV) used in this investigation. Four liters of stock solution was prepared from purified materials as follows. A weighed amount of dry malonic acid in a 4-liter flask was completely neutralized by a calculated amount of standardized sodium hydroxide (0.5 *N* and carbonate-free) added from a weight burette. Completeness of the neutralization was tested by using phenolphthalein indicator with a small measured portion of the solution. To this solution of sodium malonate, purified and standardized hydrochloric acid (0.5 *N*) was added from a weight burette, in an amount calculated to be sufficient to convert only half of the sodium malonate to sodium acid malonate and sodium chloride, according to the reaction

$$HCl+Na_2An\longrightarrow NaHAn+NaCl \qquad (13)$$

The final solution, therefore, contained equal molal quantities of NaCl, NaHAn, and Na_2An. The molality of the stock solution was calculated from the known weights of malonic acid, sodium hydroxide, hydrochloric acid, and the final weight of the solution. The molality was known with an uncertainty of not more than 0.06 percent (titration error $\approx$0.04 percent; dilution error $\approx$0.02 percent). Weights calibrated by the Mass Section of the National Bureau of Standards were used. Weighings were made in a constant temperature room at 25° C $\pm$ 0.2° C and at about 50-percent relative humidity. All weights were corrected to the "vacuum" basis.

The dissolved gases in the solutions were removed by bubbling hydrogen gas through them for 2 hours. The solutions were not boiled, because it is known that malonic acid decomposes in aqueous

solutions heated above 66° C [11]. Corrections for loss of water from the solutions during this operation were made by determining their weights before and after the deaeration.

3. APPARATUS

The apparatus employed in this investigation, including the cells, bubble tubes, electrodes, thermostat, and the emf recording instruments, were described in detail in a previous paper [4]. Suffice it to say that the cells and bubble tubes were filled under reduced pressure, the temperature of the thermostat was controlled to about 0.01° C, and the emf was measured by means of a calibrated potentiometer with galvanometer and standard cell. The emf values were corrected to 1 atmosphere of hydrogen pressure in the usual manner [12].

IV. ELECTROMOTIVE-FORCE MEASUREMENTS

The galvanic cell employed may be represented by

$$\mathrm{Pt|H_2(g)|NaHAn}(m_1),\ \mathrm{Na_2An}(m_2),\ \mathrm{NaCl}(m_3)\mathrm{|AgCl)(s)|Ag(s)}, \quad (14)$$

in which g=gas, s=solid, the vertical lines indicate the junction of two phases, and the commas indicate different components within one phase. This cell has no liquid junction; the two electrodes dip into the same solution. In this work, molality was chosen as the concentration unit (see reference [4] for other concentration units which may be used), since the value of molality is the same at all temperatures. The emf of this galvanic cell at 1 atmosphere of hydrogen pressure is given by

$$E=E^\circ-\frac{RT}{F}\ln m_{\mathrm{H}}m_{\mathrm{CL}}\gamma_{\mathrm{H}}\gamma_{\mathrm{CL}}, \quad (15)$$

in which E is the measured emf, E° the potential of the silver-silver chloride electrode measured relative to the "normal hydrogen electrode", R, T, and F have their usual meaning, and m and γ have the significance given previously in this paper.

The values of the various molalities of malonate solutions used in the galvanic cells are given in column 1 of table 1. In the other columns of this table, the emf obtained when these solutions were used in the galvanic cells are given at the designated temperatures. These values of the emf are averages of four emf measurements on the same solution, obtained as described in a previous paper [4]. The average and maximum deviations (deviations of the average emf from the four are the same within 0.01 mv at all temperatures) of individual readings of the emf from the average are listed in columns 2 and 3 of table 1. It will be noted that in all cases the maximum deviation is ±0.11 mv or less, which is equivalent to 0.0037 or less in pH units or in pK_2 values, pH being defined as the negative of the common logarithm of the hydrogen-ion activity and pK_2 as the negative of the common logarithm of the second ionization constant.

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TABLE 1.—*Average emf of four measurements of the galvanic cell* $Pt|H_2(g)|NaHAn(m_1), Na_2An(m_2), NaCl(m_3)|AgCl(s)|Ag(s)$, *from 0° to 60°C*

Concentrations of solutions	Deviation of emf from average		Temperature in degrees centigrade													
	Average	Maximum	0	5	10	15	20	25	30	35	40	45	50	55	60	
Moles of each solute per 1,000 g of water	*mv*	*mv*	*mv*	*mv*	*mv*	*mv*	*mv*	*mv*	*mv*	*mv*	*mv*	*mv*	*mv*	*mv*	*mv*	
0.0000967	0.06	0.11	703.13	708.74	714.61	720.76	727.09	733.50	739.86	745.80	751.78					
.0010619	.05	.06	701.56	707.14	713.04	719.30	725.49	731.40	737.43	743.66	750.08					
.0011095	.01	.02	700.41	706.22	712.11	718.08	724.14	730.23	736.37	742.51	748.78	755.14	761.56	767.98	774.66	
.0019114	.02	.03	696.95	692.30	697.90	703.58	709.33	715.08	720.95	726.86	732.84	738.90	745.06	751.15	757.39	
.0019420	.04	.06	696.05	691.57	697.24	702.76	708.68	714.44	720.33	726.13	732.08	738.37	744.44	750.63	756.83	
.0024182	.01	.02	690.42	685.98	691.48	697.06	702.77	708.53	714.30	720.09	725.88	731.47	737.63	743.68	749.68	
.0029126	.02	.02	675.80	681.15	686.65	692.17	697.71	703.29	708.95	714.67	720.45					
.0030385	.02	.03	674.54	679.93	685.38	690.76	696.31	701.95	707.44	713.09	718.84	724.60	730.54	736.44	742.54	
.0040020	.01	.02	667.61	672.85	678.19	683.56	689.03	694.42	699.93	705.32	710.79	716.54	722.12	727.68	733.34	
.0047661	.03	.04	663.26	668.41	673.62	678.86	684.16	689.45	694.84	700.20	705.65	711.04	716.53	722.32	727.94	
.0050248	.01	.02	661.45	666.54	671.72	676.98	682.33	687.67	693.10	698.55	704.16					
.0068161	.03	.05	653.84	658.87	664.00	669.01	674.05	679.21	684.35	689.54	694.76	700.00	705.16	710.75	716.17	
.0068596	.01	.02	653.39	658.29	663.34	668.45	673.67	678.77	683.98	689.19	694.52	699.82	705.25	710.82	716.70	
.0094543	.02	.02	645.06	649.92	654.82	659.70	664.60	669.57	674.56	679.59	684.67	689.81	694.97	700.19	705.38	
.0095398	.01	.02	644.78	649.42	654.39	659.16	664.26	669.23	674.30	679.36	684.43	689.42	694.87	699.99	705.09	
.018622	.01	.02	626.64	631.14	635.62	640.23	644.78	649.30	654.00	658.64	663.36	668.00	672.74	677.42	682.17	
.029535	.01	.02	613.93	618.16	622.46	626.74	631.01	635.40	639.71	644.11	648.50	652.84	657.25	661.72	666.24	
.044566	.01	.02	602.30	606.29	610.37	614.42	618.48	622.63	626.74	630.85	635.01	639.19	643.40	647.60	651.87	

V. CALCULATION OF THE SECOND IONIZATION CONSTANT OF MALONIC ACID

The second ionization constant of malonic acid is calculated for each temperature by means of eq 6,[7] which defines the constant in terms of the ionic activities, and by eq 15, which gives the hydrogen-ion activity in terms of the measured emf. Upon solving for the hydrogen-ion molality in these two equations, converting to common logarithms, and rearranging, the equations

$$-\log m_{\mathrm{H}} = -\log K_2 - \log \frac{m_{\mathrm{HAn}}}{m_{\mathrm{An}}} - \log \frac{\gamma_{\mathrm{HAn}}}{\gamma_{\mathrm{H}}\gamma_{\mathrm{An}}} \tag{16}$$

and

$$-\log m_{\mathrm{H}} = \frac{(E-E^0)F}{2.3026RT} + \log m_{\mathrm{Cl}} + \log \gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}} \tag{17}$$

result. Elimination of $-\log m_{\mathrm{H}}$ from these equations and rearrangement, keeping all the measured quantities on the left side, gives

$$\frac{(E-E^0)F}{2.3026RT} + \log m_{\mathrm{Cl}} + \log \frac{m_{\mathrm{HAn}}}{m_{\mathrm{An}}} = -\log K_2 - \log \frac{\gamma_{\mathrm{Cl}}\gamma_{\mathrm{HAn}}}{\gamma_{\mathrm{An}}}. \tag{18}$$

All terms on the left side of this equation are known from experiment, hence values of $-\log K_2 - \log \gamma_{\mathrm{Cl}}\gamma_{\mathrm{HAn}}/\gamma_{\mathrm{An}}$ may be obtained for various molalities of malonate solutions. The logarithm of the ratio containing the activity coefficients becomes zero at infinite dilution or at zero ionic strength (see footnote 4). Hence, if values of the left side of eq 18 for various molalities are plotted against the ionic strength, extrapolation gives the value of $-\log K_2$ at the intercept at zero ionic strength. Extrapolation can be made with more certainty by using the equations of Debye and Hückel [13].

Debye and Hückel, from theoretical considerations of the electrostatic forces between positive and negative ions and assuming that the ions are point charges, obtained the equation [8]

$$\log \gamma_i = -Az^2{}_i\sqrt{\mu} \tag{19}$$

for the activity coefficient of an ion in terms of the ionic strength of the solution, μ, its valence, z_i, and a general constant, A.[9] Experi-

[7] To illustrate the method of calculating the constant, eq 6 is used here instead of eq 8. For accurate results, the latter is used. The H^+ corrections in eq 8 are obtained by successive approximations in the following manner. After K_2 has been obtained by eq 18, and neglecting these corrections, it is used in eq 8 and calculations made of H^+. These values of H^+ are then used in eq 18 to correct m_{HAn} and m_{An}, and new values of K_2 are then calculated. This arithmetical procedure is repeated until values of K_2 and H^+ are consistent. Since H^+ values are so low for the solutions investigated here, only one approximation of this type is required.

[8] In the original derivation, Debye and Hückel used concentrations in terms of moles of solute per liter of solution. In this work, because of investigations at different temperatures, concentrations in terms of moles of solute per 1,000 g of water, or molality, were employed because the values of molality do not change with a change in temperature. For dilute solutions, these terms become very nearly the same. It is of interest to note that Scatchard, Chem. Rev. **19**, 309 (1936) states that molality should be used in the Debye-Hückel equation instead of concentration as originally done by Debye and Hückel.

[9] The general constants, A and B, used in eq 19, 20, 21, 22, 23, 24, 25, 26, and 28 are defined by

$$A = \frac{\sqrt{2\pi}}{2.3026}\left(\frac{\epsilon^2}{\sqrt{Dk(t+T_0)}}\right)^3\left(\frac{N}{1000}\right)^{1/2}$$

and

$$B = \frac{4.6052Dk(t+T_0)}{\epsilon^2}A,$$

where ϵ is the electronic charge, N the Avogadro number, D the dielectric constant of water, k the Boltzmann constant, t the temperature of the solutions in degrees centigrade, and T_0 the temperature of the ice point in degrees Kelvin.

mental evidence [14] has shown that this equation is valid only for very dilute solutions, 0.01 M or less, and to extend its range of application it is necessary to add a term $\lambda\mu$ to the right side of eq 19. λ is an empirical constant, the value of which must be determined from experiments, and is the slope of the straight-line portion of curve A, figure 1. Making this correction in eq 19 and substituting eq 19 for each activity coefficient term in eq 18 and transposing all known values to the left gives

$$\frac{(E-E^0)F}{2.3026RT}+\log m_{Cl}+\log\frac{m_{HAn}}{m_{An}}+2A\sqrt{\mu}=-\log K_2-\lambda\mu. \quad (20)$$

Later, Debye and Hückel modified their equation to take into account the closest distance of approach of the ions, a_i, and obtained

$$\log\gamma_i=-\frac{Az_i'\sqrt{\mu}}{1+Ba_i\sqrt{\mu}} \quad (21)$$

where B is a general constant. Experimental evidence [14] and theoretical considerations by Hückel [13] have shown that this form of equation is valid for solutions about 0.05 M or less, provided the proper value of a_i is used. If an approximate value of a_i is employed, it is necessary to add a term $\beta\mu$ to the right side of eq 21. β is an empirical constant, the value of which must be determined from experiments, and is the slope of the straight-line portion of curve B, figure 1. Guggenheim [15] suggested using 3 angstrom units for a_i. Ba_i is then approximately equal to unity. Using this approximate value for a_i and also using $\beta\mu$, eq 21 becomes

$$\log\gamma i=-\frac{Az_i'\sqrt{\mu}}{1+\sqrt{\mu}}+\beta\mu \quad (22)$$

Substituting this equation for each activity coefficient term in eq 18 and transposing all known terms to the left gives

$$\frac{(E-E^0)F}{2.3026RT}+\log m_{Cl}+\log\frac{m_{HAn}}{m_{An}}+\frac{2A\sqrt{\mu}}{1+\sqrt{\mu}}=-\log K_2-\beta\mu. \quad (23)$$

There are, therefore, three expressions (eq 18, 20, and 23) which are functions of $-\log K_2$, all of which become equal to $-\log K_2$ at zero ionic strength. Using the molalities and the emf given in table 1, values of the ionic strength given by $(m_1+3m_2+m_3+2m_H)$, and the general constants given in table 2, values of the left sides of eq 18, 20, and 23 were calculated for each molality of the malonate solutions at 25° C and are given in table 3.

TABLE 2.—*Numerical values of constants at temperatures from 0° to 60° C used for calculations of the second ionization constant of malonic acid and the* pH *values of malonate solutions*

Temperature, t	$\frac{2.3026RT}{F}$	E^0, the normal potential of the silver-silver chloride electrode [1]	D, the dielectric constant of water [3]	A, the Debye-Hückel constant [3]	B, a constant in the Debye-Hückel equation	a_i, the average distance of approach of the ions	$B \times a_i$
°C	v	v			*Reciprocal* Å	Å	
0	0.05420	0.23644	88.15	0.4890	0.3253	4.99	1.62
5	.05519	.23396	86.12	.4928	.3261	4.98	1.62
10	.05618	.23132	84.15	.4967	.3270	4.96	1.62
15	.05717	.22846	82.23	.5009	.3279	4.89	1.60
20	.05816	.22550	80.36	.5053	.3289	4.81	1.58
25	.05916	.22238	78.54	.5098	.3298	4.75	1.57
30	.06015	.21911	76.76	.5147	.3309	4.64	1.54
35	.06114	.21564	75.03	.5197	.3320	4.53	1.50
40	.06213	.21207	73.35	.5250	.3330	4.42	1.47
45	.06313	.20822	71.70	.5303	.3342	4.29	1.43
50	.06412	.20432	70.10	.5358	.3353	4.12	1.38
55	.06511	.20033	68.53	.5417	.3366	3.96	1.33
60	.06610	.19619	67.00	.5478	.3378	3.76	1.27

[1] These values were calculated from the emf data obtained by Harned and Ehlers, J. Am. Chem. Soc. **54,** 1350 (1932); **55,** 652, 2179 (1933), using the numerical values of R, T_0, F, k, and ϵ given by Wensel, the numerical values of D given by the equation of Wyman and Ingalls, and the densities of HCl solutions given in the Int. Crit. Tables, **3,** 54 (1928). Values of E^0 were obtained by the method of Harned and Ehlers, except that the method of least squares was used instead of a graphical method (data below 0.03 M HCl were employed). These values agree with the values reported by Harned and Ehlers within 0.1 mv.

[3] Values of D were calculated from the equation of Wyman and Ingalls, J. Am. Chem. Soc. **60,** 1182 (1938). This equation is $D=78.54[1-4.579\times10^{-3}(t-25)+1.19\times10^{-5}(t-25)^2-2.8\times10^{-8}(t-25)^3]$.

[3] Values of A were calculated, using $R=8.3142$ absolute joules deg^{-1} mole^{-1}, $F=96{,}490$ absolute coulomb mole^{-1}; $\epsilon=4.800\times10^{-10}$ esu; $k=1.380\times10^{-16}$ erg deg^{-1}; and $T_0=273.16°$ K, given by Wensel, J. Research NBS **22,** 375 (1939) RP1189. The value of $N=6.026\times10^{23}$ was obtained by the relation $N=Fc/\epsilon$, where $c=2.99776\times10^{10}$ cm sec^{-1}, the velocity of light or the conversion factor between electrostatic and electromagnetic units. E and E^0 were measured in international volt and were converted to absolute units for subsequent calculations.

TABLE 3.—*Values of the left sides of eq 18, 20, 23, and 25 at 25° C for different molalities of sodium malonate solutions*

Concentration of solutions	Values of the left side of eq 18	Values of the left side of eq 20	Values of the left side of eq 23	Values of the left side of eq 25	Estimated uncertainties in these values corresponding to the maximum deviations in the emf [1]
Moles of each solute per 1,000 g of water					
0.0009867	5.6328	5.7039	5.6993	5.6969	0.0037
.0010619	5.6293	5.7031	5.6982	5.6956	.0020
.0011095	5.6287	5.7041	5.6989	5.6984	.0004
.0019114	5.6096	5.7085	5.6998	5.6955	.0009
.0019420	5.6057	5.7054	5.6966	5.6922	.0022
.0024182	5.6012	5.7125	5.7016	5.6963	.0007
.0029128	5.5935	5.7159	5.7028	5.6964	.0005
.0030385	5.5893	5.7141	5.7006	5.6940	.0011
.0040020	5.5818	5.7250	5.7075	5.6993	.0007
.0047561	5.5729	5.7290	5.7083	5.6987	.0015
.0050248	5.5666	5.7271	5.7054	5.6953	.0007
.0068161	5.5561	5.7431	5.7143	5.6914	.0018
.0068596	5.5515	5.7390	5.7100	5.6970	.0006
.0094543	5.5353	5.7555	5.7167	5.6985	.0005
.0095398	5.5335	5.7547	5.7155	5.6981	.0005
.018622	5.4887	5.7977	5.7261	5.6959	.0005
.029535	5.4525	5.8417	5.7348	5.6906	.0005
.044566	5.4154	5.8934	5.7426	5.6961	.0007

[1] These uncertainties are the same for all temperatures from 0° to 60° C.

It will be seen that the values calculated in molality terms alone by eq 18 (column 2, table 3) are different for the various values of the molality; hence a conversion to activity units must be made. In column 3, values obtained by using the Debye-Hückel equation, in which ions are assumed to be point charges, are given. These likewise vary with molality, but in opposite direction from those obtained in molality units, indicating that the Debye-Hückel equation gives too large a correction. In column 4 are given the values obtained by eq 23, assuming the closest distance of approach of the ions to be 3 Å. These values show a variation with molality which is smaller than the one obtained by assuming that the ions are point charges. In figure 1 these three sets of values are shown plotted against the ionic

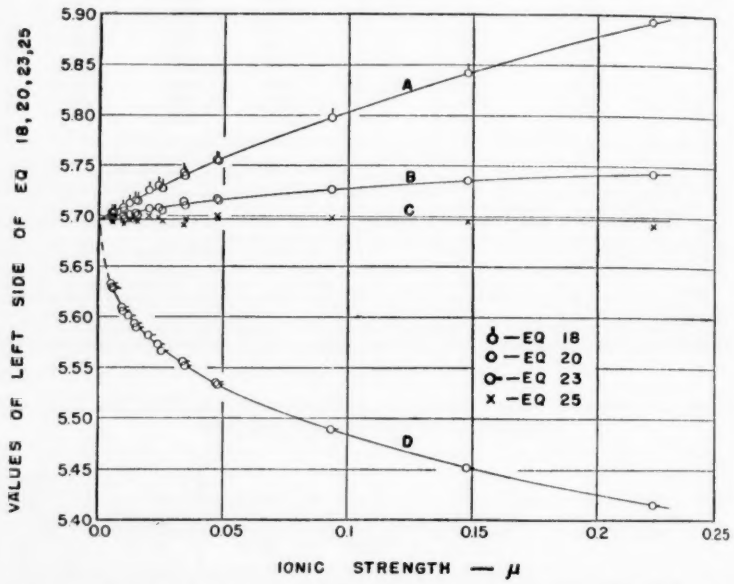

FIGURE 1.—*Plots of the values of the left sides of equations 18, 20, 23, and 25 for different molalities of solutions of sodium malonate salts against the ionic strength, at 25° C.*

strength. It will be noted that all three sets converge to the same point at zero ionic strength, at which point the value of $-\log K_2$ is obtained. Extrapolation of the lower curve, *D*, is difficult, but extrapolation of the upper two curves, *A* and *B*, to zero ionic strength may be made with certainty. To insure better extrapolation, the method of least squares was employed.[10] By this method, a value of 5.6959

[10] Values for the three most concentrated solutions were not used. The others are all on a straight line within the experimental error, and the method of least squares was used with a linear equation through these points.

was obtained for $-\log K_2$ from the top curve, A, and a value of 5.6960 was obtained for $-\log K_2$ from the second curve, B. Since these two curves give identical values of $-\log K_2$, it is of interest to see if a value may be obtained for a_i which, when used to calculate $-\log K_2$, will give the same value at all the molalities of malonate solutions. Substituting eq 21 for each activity coefficient term in eq 18 and solving for a_i, we have

$$a_i = -\frac{1}{B\sqrt{\mu}} - \frac{2A}{B[\log m_{Cl} + \log K_2 + \log (m_{HAn}/m_{An}) + (E - E^0)F/2.3026RT]}. \quad (24)$$

By using the values of B given in column 6 of table 2, the value of $-\log K_2$ given above, the molalities of the solutions, and the emf, values of a_i were calculated for 25° C for each value of μ and averaged, the average value being 4.75 A. This value of a_i is an average value for the distance of approach of the ions, the H^+ ion being excepted. Using this value of a_i in eq 21 and substituting this equation for each activity coefficient term in eq 18, we have

$$\frac{(E - E^0)F}{2.3026RT} + \log m_{Cl} + \log \frac{m_{HAn}}{m_{An}} + \frac{2A\sqrt{\mu}}{1 + 4.75B\sqrt{\mu}} = -\log K_2. \quad (25)$$

Values of $-\log K_2$ were then calculated for each molality of the malonate solutions by this equation. The values are given in column 5 of table 3 and are shown plotted against the ionic strength in figure 1, curve C. These values are the same, within the experimental error, at all molalities, and eq 25, therefore, gives the same values of $-\log K_2$ at all ionic strengths from 0 to 0.22 for 25° C. In the last column of table 3, the uncertainties in all four sets of values which arise from the maximum deviations in the emf are given.

Similar calculations were made for the other temperatures. In table 4, values of the left side of eq 20 are given for all the temperatures, and are shown plotted against the ionic strength in figure 2 for 0°, 25°, 45°, and 60° C. In table 5, values of the left side of eq 23 are given for all the temperatures, and are shown plotted against the ionic strength in figure 3. Values of $-\log K_2$ were obtained at each temperature from these two sets of values by the method of least squares, as described above for 25° C. Values thus obtained are given in columns 2 and 3 of table 6. It will be seen that the two sets of values of $-\log K_2$ are in close agreement. In column 4, the average of these values with the limits of uncertainty is given for each temperature. In column 5, values of K_2, or the second ionization constant of malonic acid, are listed. Columns 6 and 7 give the limits of uncertainty in K_2; the sixth gives the uncertainty due to extrapolation and the seventh gives the total uncertainty arising from the errors in the molality, the ionic strength, extrapolation, and the emf.

TABLE 4.—*Values of the left side of eq 20 from 0° to 60° C for different molalities of sodium malonate solutions*

[Ions are assumed to be point charges—Debye and Hückel]

Concentration of solutions	Temperature in degrees centigrade												
	0	5	10	15	20	25	30	35	40	45	50	55	60
Moles of each solute per 1,000 g of water													
0.0009867	5.6741	5.6639	5.6646	5.6726	5.6864	5.7039	5.7211	5.7361	5.7533				
.0010619	5.6797	5.6696	5.6714	5.6818	5.6937	5.7031	5.7184	5.7357	5.7605				
.0011095	5.6793	5.6736	5.6756	5.6812	5.6911	5.7041	5.7186	5.7377	5.7605	5.7870	5.8129	5.8421	5.8765
.0019114	5.6906	5.6812	5.6827	5.6877	5.6969	5.7085	5.7230	5.7427	5.7653	5.7911	5.8109	5.8456	5.8774
.0019420	5.6816	5.6757	5.6786	5.6810	5.6935	5.7054	5.7204	5.7385	5.7608	5.7904	5.8153	5.8453	5.8768
.0024182	5.6843	5.6812	5.6828	5.6882	5.6987	5.7125	5.7273	5.7469	5.7683	5.7886	5.8167	5.8463	5.8765
.0029128	5.6906	5.6852	5.6885	5.6945	5.7032	5.7159	5.7304	5.7505	5.7730				
.0030385	5.6885	5.6838	5.6867	5.6906	5.7003	5.7141	5.7262	5.7455	5.7682	5.7931	5.8196	5.8488	5.8821
.0040020	5.6978	5.6932	5.6965	5.7026	5.7132	5.7250	5.7397	5.7570	5.7774	5.8043	5.8275	5.8537	5.8827
.0047561	5.7051	5.7003	5.7028	5.7080	5.7173	5.7290	5.7432	5.7615	5.7831	5.8064	5.8295	5.8602	5.8900
.0050248	5.6906	5.6945	5.6971	5.7034	5.7141	5.7271	5.7425	5.7628	5.7875				
.0068161	5.7172	5.7136	5.7181	5.7225	5.7305	5.7431	5.7563	5.7750	5.7954	5.8193	5.8405	5.8718	5.9026
.0068596	5.7122	5.7065	5.7096	5.7161	5.7256	5.7390	5.7535	5.7726	5.7955	5.8199	5.8453	5.8762	5.9128
.0094543	5.7293	5.7259	5.7292	5.7345	5.7431	5.7555	5.7693	5.7883	5.8100	5.8347	5.8588	5.8872	5.9167
.0095398	5.7290	5.7217	5.7265	5.7300	5.7421	5.7547	5.7699	5.7895	5.8111	5.8335	5.8622	5.8891	5.9171
.018622	5.7693	5.7660	5.7686	5.7758	5.7849	5.7977	5.8117	5.8308	5.8531	5.8763	5.9003	5.9268	5.9558
.029535	5.8123	5.8088	5.8129	5.8189	5.8280	5.8417	5.8557	5.8753	5.8969	5.9200	5.9415	5.9698	6.0018
.044566	5.8618	5.8584	5.8630	5.8694	5.8793	5.8934	5.9082	5.9277	5.9500	5.9751	6.0000	6.0283	6.0591

TABLE 5.—*Values of the left side of eq 23 from 0° to 60° C for different molalities of sodium malonate solutions* [1]

[Closest distance of approach of the ions is assumed to be 3 A—Guggenheim]

Concentration of solutions	Temperature in degrees centigrade												
	0	5	10	15	20	25	30	35	40	45	50	55	60
Moles of each solute per 1,000 g of water													
0.0009867	5.6697	5.6598	5.6601	5.6681	5.6818	5.6993	5.7164	5.7312	5.7485				
.0010619	5.6750	5.6648	5.6665	5.6759	5.6887	5.6982	5.7104	5.7306	5.7556				
.0011095	5.6743	5.6686	5.6700	5.6758	5.6860	5.6989	5.7133	5.7334	5.7553	5.7814	5.8073	5.8365	5.8708
.0019114	5.6823	5.6729	5.6742	5.6792	5.6882	5.6998	5.7142	5.7438	5.7562	5.7818	5.8016	5.8361	5.8679
.0019420	5.6732	5.6662	5.6700	5.6724	5.6847	5.6966	5.7115	5.7294	5.7516	5.7810	5.8058	5.8357	5.8670
.0024182	5.6739	5.6706	5.6722	5.6775	5.6869	5.7016	5.7163	5.7358	5.7570	5.7770	5.8050	5.8345	5.8644
.0029128	5.6781	5.6716	5.6757	5.6816	5.6906	5.7028	5.7171	5.7370	5.7593				
.0030385	5.6752	5.6708	5.6736	5.6774	5.6869	5.7006	5.7125	5.7316	5.7542	5.7788	5.8051	5.8341	5.8673
.0040020	5.6811	5.6763	5.6795	5.6854	5.6959	5.7075	5.7220	5.7390	5.7592	5.7858	5.8087	5.8346	5.8633
.0047561	5.6855	5.6805	5.6829	5.6880	5.6970	5.7083	5.7223	5.7403	5.7617	5.7840	5.8089	5.8378	5.8673
.0050248	5.6790	5.6737	5.6761	5.6822	5.6926	5.7054	5.7206	5.7406	5.7649				
.0068161	5.6898	5.6860	5.6902	5.6944	5.7020	5.7143	5.7272	5.7453	5.7660	5.7889	5.8097	5.8405	5.8698
.0068596	5.6847	5.6787	5.6816	5.6778	5.6969	5.7100	5.7242	5.7429	5.7654	5.7893	5.8143	5.8448	5.8811
.0094543	5.6923	5.6886	5.6916	5.6965	5.7047	5.7167	5.7290	5.7483	5.7696	5.7927	5.8172	5.8451	5.8736
.0095398	5.6917	5.6841	5.6885	5.7036	5.7034	5.7155	5.7303	5.7493	5.7704	5.7922	5.8203	5.8466	5.8739
.018622	5.7013	5.6975	5.6994	5.7059	5.7142	5.7261	5.7395	5.7575	5.7789	5.8010	5.8239	5.8493	5.8771
.029535	5.7104	5.7061	5.7093	5.7143	5.7222	5.7348	5.7473	5.7656	5.7859	5.8074	5.8294	5.8557	5.8841
.044566	5.7170	5.7125	5.7159	5.7209	5.7291	5.7426	5.7547	5.7721	5.7925	5.8153	5.8380	5.8639	5.8922

[1] Acknowledgment is made to J. H. Payne, Student Assistant, summers of 1937 and 1938, for aid in calculations of the data in this table.

TABLE 6.—*Negative of the common logarithm and the numerical values of the second ionization constant of malonic acid from 0° to 60° C, as obtained by two different functions (Debye-Hückel and Guggenheim)*

Temperature, t	Values of $-\log K_2$ obtained from the values of the left side of eq 20	Values of $-\log K_2$ obtained from the values of the left side of eq 23	Average values of $-\log K_2$ and limits of uncertainty	Values of the second ionization constant of malonic acid, K_2	Uncertainty in K_2 arising from the two methods used to solve for $-\log K_2$	Total estimated uncertainty in K_2 arising from known uncertainties in emf, concentration, ionic strength, and extrapolation
°C				$K_2 \times 10^6$		
0	5.6699	5.6693	5.6696 ±0.0003	2.140	±0.002	±0.006
5	5.6641	5.6651	5.6646 ± .0005	2.165	.003	.007
10	5.6667	5.6675	5.6671 ± .0004	2.152	.002	.006
15	5.6723	5.6734	5.6729 ± .0005	2.124	.003	.006
20	5.6825	5.6830	5.6828 ± .0003	2.076	.002	.006
25	5.6959	5.6960	5.6960 ± .0001	2.014	.001	.006
30	5.7101	5.7107	5.7104 ± .0003	1.948	.001	.006
35	5.7294	5.7299	5.7297 ± .0003	1.863	.001	.006
40	5.7521	5.7529	5.7525 ± .0004	1.768	.002	.005
45	5.7772	5.7771	5.7772 ± .0001	1.670	.001	.006
50	5.8021	5.8030	5.8026 ± .0005	1.575	.001	.005
55	5.8333	5.8329	5.8331 ± .0002	1.469	.001	.005
60	5.8664	5.8652	5.8658 ± .0006	1.362	.002	.005

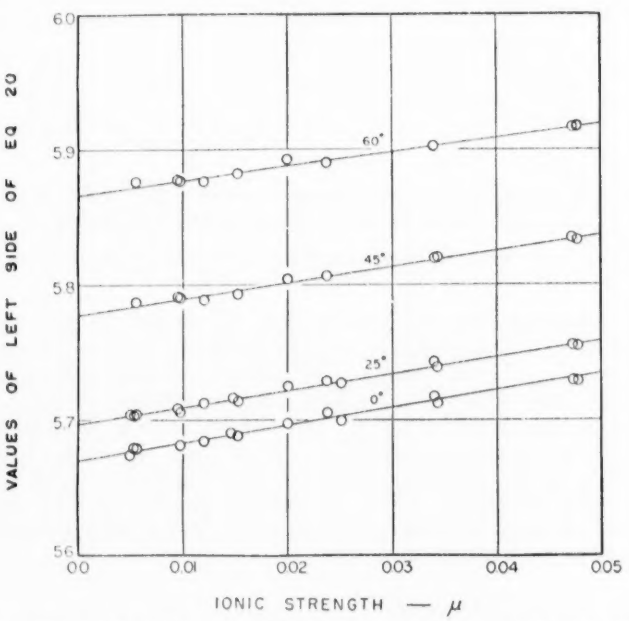

FIGURE 2.—*Plots of the values of the left side of equation 20 for different molalities of solutions of sodium malonate salts against the ionic strength at 0, 25, 45, and 60° C.*

Ions are assumed to be point charges (Debye-Hückel).

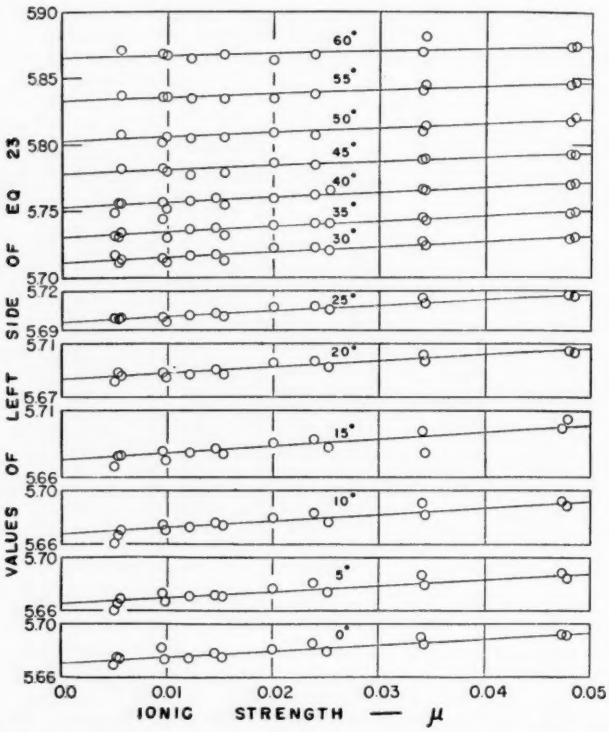

FIGURE 3.—*Plots of the values of the left side of equation 23 for different molalities of solutions of sodium malonate salts against the ionic strength.*

Three angstrom units was used for the average ionic diameter in the expressions for the activity coefficients (Guggenheim).

These values of $-\log K_2$ were used in eq 24 to calculate values of a_i for the different temperatures, as was done for 25° C. Values thus calculated are given in column 7 of table 2. These values are then used to calculate values of $-\log K_2$ at all the molalities of the malonate solutions, as was done for 25° C, and the values are given in table 7. It will be seen that these values of $-\log K_2$ are the same, within the experimental error, at all molalities, indicating that proper values of a_i have been obtained. They are shown plotted against the ionic strength at all the temperatures in figure 4. Values of a_i decrease with an increase in the temperature.

TABLE 7.—*Negative of the common logarithm of the second ionization constant of malonic acid from 0° to 60° C and at various molalities of solutions of malonate salts, calculated with use of the values for the average ionic diameters given in column 7 of table 2 in expressions for activity coefficients*

Concentration of solutions	Temperature in degrees centigrade												
	0	5	10	15	20	25	30	35	40	45	50	55	60
Moles of each solute per 1,000 g of water													
0.0009867	5.6671	5.6572	5.6575	5.6655	5.6793	5.6969	5.7141	5.7291	5.7465				
.0010619	5.6722	5.6620	5.6637	5.6742	5.6860	5.6956	5.7079	5.7283	5.7534				
.0011095	5.6711	5.6657	5.6676	5.6729	5.6832	5.6984	5.7108	5.7300	5.7530	5.7793	5.8054	5.8348	5.8695
.0019114	5.6775	5.6681	5.6694	5.6746	5.6837	5.6955	5.7100	5.7298	5.7515	5.7784	5.7985	5.8334	5.8665
.0019420	5.6684	5.6624	5.6652	5.6677	5.6801	5.6922	5.7072	5.7254	5.7478	5.7776	5.8027	5.8330	5.8648
.0024182	5.6681	5.6647	5.6663	5.6718	5.6824	5.6963	5.7111	5.7309	5.7524	5.7738	5.8012	5.8312	5.8617
.0029128	5.6712	5.6656	5.6688	5.6749	5.6840	5.6964	5.7110	5.7312	5.7538				
.0030385	5.6681	5.6637	5.6664	5.6704	5.6801	5.6940	5.7062	5.7256	5.7485	5.7736	5.8005	5.8300	5.8640
.0040020	5.6721	5.6673	5.6705	5.6766	5.6873	5.6993	5.7140	5.7314	5.7520	5.7792	5.8028	5.8295	5.8592
.0047561	5.6750	5.6701	5.6724	5.6778	5.6870	5.6987	5.7131	5.7316	5.7533	5.7763	5.8000	5.8319	5.8624
.0050248	5.6681	5.6628	5.6651	5.6715	5.6822	5.6953	5.7109	5.7314	5.7562				
.0068161	5.6758	5.6720	5.6761	5.6806	5.6886	5.6914	5.7147	5.7336	5.7548	5.7786	5.8005	5.8324	5.8633
.0068596	5.6706	5.6646	5.6674	5.6739	5.6835	5.6970	5.7117	5.7310	5.7541	5.7789	5.8051	5.8367	5.8745
.0094543	5.6732	5.6703	5.6733	5.6777	5.6873	5.6998	5.7138	5.7330	5.7550	5.7803	5.8052	5.8345	5.8651
.0095398	5.6734	5.6657	5.6701	5.6737	5.6859	5.6985	5.7139	5.7338	5.7557	5.7786	5.8082	5.8360	5.8652
.018622	5.6711	5.6672	5.6690	5.6762	5.6853	5.6981	5.7124	5.7318	5.7545	5.7785	5.8038	5.8317	5.8626
.029535	5.6687	5.6643	5.6673	5.6733	5.6823	5.6959	5.7099	5.7301	5.7521	5.7762	5.8015	5.8312	5.8639
.044566	5.6626	5.6580	5.6612	5.6674	5.6769	5.6906	5.7058	5.7260	5.7483	5.7743	5.8012	5.8316	5.8655
Average	5.6708	5.6651	5.6676	5.6733	5.6836	5.6961	5.7110	5.7302	5.7524	5.7774	5.8026	5.8327	5.8649
Average deviation	0.0027	0.0029	0.0027	0.0029	0.0025	0.0020	0.0022	0.0019	0.0022	0.0018	0.0021	0.0017	0.0025

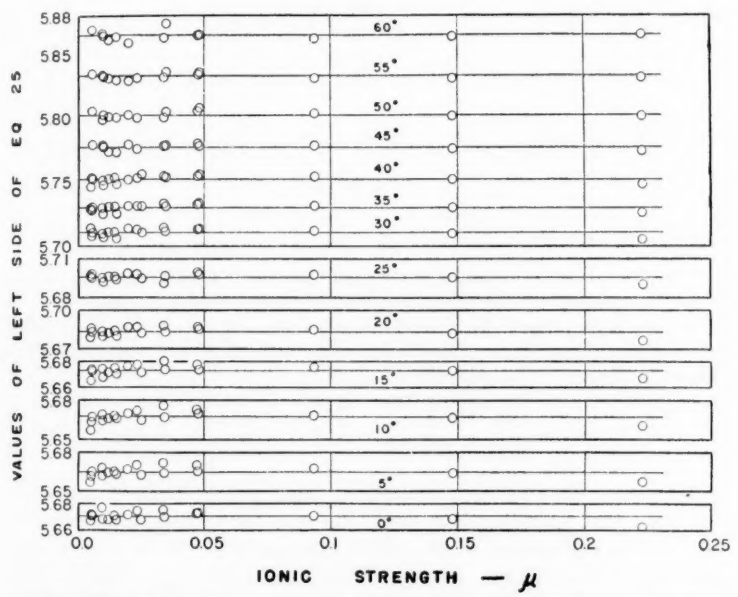

FIGURE 4.—*Plots of the values of $-\log K_2$ calculated by equation 25 for different molalities of solutions of sodium malonate salts against the ionic strength at temperatures from 0° to 60° C.*

Closest distance of approach of the ions at the different temperatures are given in column 7 of table 2.

The magnitude of the second ionization constant of malonic acid is different at the various temperatures. The maximum value is at a temperature of about 6° C. This variation is similar to that found for a number of other weak electrolytes [16]. Since K_2 expresses the ionization of the HAn^- ion into H^+ and $An^=$ ions, the HAn^- ionizes less at the higher temperatures, giving less H^+ ions and, therefore, decreased acidity.

In table 8 the previous values found at 18° and 25° C, as well as the corresponding ones obtained in this investigation, are listed. The table is self-explanatory.

TABLE 8.—*Values of the second ionization constant of malonic acid obtained by different workers at 18° and 25° C*

a, Estimated values.
b, Values include approximations.
c, Values include salt errors.
d, Values include values of liquid-junction potentials.
e, Empirical method used in calculation of the values.
f, Values include errors of quinhydrone electrode. (See Hovorka and Dearing, J. Am. Chem. Soc. **57**, 446 (1935), for a study of "salt errors" of the quinhydrone electrode.)

Year	Observer	Method	$K_2 \times 10^6$		Note on the values
			18° C	25° C	
1898	Smith	Sucrose inversion		1.0	*a*
1902–05	Wegscheider	Conductivity		10.0	*a*
1908	Chandler	Partition		2.03	*b*
1908	do	Conductivity		2.1	*b*
1915	Datta and Dhar	CO_2 absorption		1.36	*b*
1916	Wegscheider	Conductivity		1.0	*a*
1924	Larsson	Potentiometric titration	2.0		*c,e*
1925	Britton	do	4.45		*c,d,e*
1928	Simms	do		1.8	*d,e*
1928	Gane and Ingold	do		4.37	*c,d*
1931	do	do		2.03	*d*
1933	Burton	do		3.89	*b,c,d*
1936	Burton, Hamer, and Acree	do		2.94	*c,d*
1936	Hamer and Acree	do		2.51	*d*
1936	German and Vogel	do		2.20	*c,f*
1940	Hamer, Burton, and Acree	Galvanic cells without liquid junctions.	* 2.102	2.014	

* Value calculated by eq 32.

VI. pH AND pH EQUATIONS

In a previous paper [4] it was shown how the pH value of a solution may be calculated from the measurements of galvanic cells without liquid junctions. The equation

$$\mathrm{pH}=\frac{(E-E^0)F}{2.3026RT}+\log m_{\mathrm{Cl}}-\frac{A\sqrt{\mu}}{1+Ba_i\sqrt{\mu}}+\beta\mu \qquad (26)$$

was derived. It was also stated in that paper that if values of a_i and β were not known, they could be obtained from a detailed study of the thermodynamics of solutions, considerations of interactions of ions, or by other means. In this paper it has been shown how accurate values of a_i may be obtained from values of the ionization constant. It follows that with the use of these value of a_i, β has a value of zero (see section V). Using the values of a_i and Ba_i given in table 2, the pH values of the malonate solutions here investigated were calculated by eq 26 and are given in table 9. The uncertainties in these pH values are the same as those given in the last column of table 3. The

pH of the malonate solutions is lower at the higher concentrations, mainly because of the increase in the salt concentration and interionic attraction given by the $-A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})$ term. These solutions are suitable as buffer solutions, because the change is small.

TABLE 9.—pH *values of malonate solutions from 0° to 60° C, calculated with use of the values for the closest distance of approach of the ions given in column 7 of table 2 in the expressions for activity coefficients* [1]

Concentration of solutions	Temperature in degrees centigrade												
	0	5	10	15	20	25	30	35	40	45	50	55	60
Moles of each solute per 1,000 g of water													
.0009867	5. 5774	5. 5670	5. 5666	5. 5739	5. 5866	5. 6030	5. 6191	5. 6328	5. 6588				
.0010619	5. 5783	5. 5685	5. 5695	5. 5782	5. 5899	5. 6069	5. 6095	5. 6286	5. 6523				
.0011095	5. 5765	5. 5703	5. 5714	5. 5763	5. 5851	5. 5970	5. 6103	5. 6281	5. 6497	5. 6745	5. 6989	5. 7265	5. 7592
.0019114	5. 5556	5. 5455	5. 5458	5. 5500	5. 5576	5. 5679	5. 5798	5. 5989	5. 6198	5. 6437	5. 6616	5. 6941	5. 7238
.0019420	5. 5456	5. 5389	5. 5407	5. 5422	5. 5530	5. 5637	5. 5771	5. 5936	5. 6152	5. 6419	5. 6647	5. 6927	5. 7219
.0024182	5. 5129	5. 5287	5. 5293	5. 5336	5. 5425	5. 5547	5. 5678	5. 5856	5. 6001	5. 6232	5. 6491	5. 6764	5. 7041
.0029128	5. 5248	5. 5183	5. 5203	5. 5251	5. 5323	5. 5431	5. 5557	5. 5738	5. 5942				
.0030385	5. 5190	5. 5137	5. 5152	5. 5179	5. 5258	5. 5379	5. 5480	5. 5653	5. 5859	5. 6084	5. 6324	5. 6590	5. 6897
.0040020	5. 5047	5. 4990	5. 5008	5. 5055	5. 5140	5. 5238	5. 5363	5. 5513	5. 5693	5. 5935	5. 6138	5. 6370	5. 6628
.0047461	5. 4955	5. 4894	5. 4903	5. 4941	5. 5010	5. 5105	5. 5224	5. 5382	5. 5571	5. 5768	5. 5969	5. 6248	5. 6512
.0050248	5. 4845	5. 4781	5. 4790	5. 4837	5. 4910	5. 5029	5. 5159	5. 5336	5. 5555				
.0068161	5. 4687	5. 4637	5. 4661	5. 4688	5. 4740	5. 4841	5. 4945	5. 5101	5. 5279	5. 5478	5. 5652	5. 5925	5. 6181
.0068596	5. 4630	5. 4557	5. 4569	5. 4616	5. 4683	5. 4792	5. 4909	5. 5070	5. 5266	5. 5475	5. 5692	5. 5961	5. 6287
.0094543	5. 4397	5. 4345	5. 4356	5. 4387	5. 4441	5. 4535	5. 4640	5. 4794	5. 4974	5. 5180	5. 5376	5. 5613	5. 5856
.0095398	5. 4382	5. 4290	5. 4316	5. 4329	5. 4419	5. 4514	5. 4633	5. 4793	5. 4972	5. 5154	5. 5397	5. 5618	5. 5848
.018622	5. 3731	5. 3673	5. 3668	5. 3809	5. 3756	5. 3843	5. 3936	5. 4078	5. 4249	5. 4423	5. 4600	5. 4799	5. 5017
.029535	5. 3229	5. 3164	5. 3167	5. 3190	5. 3225	5. 3311	5. 3390	5. 3521	5. 3678	5. 3836	5. 3993	5. 4189	5. 4401
.044566	5. 2720	5. 2650	5. 2651	5. 2655	5. 2700	5. 2779	5. 2856	5. 2976	5. 3120	5. 3282	5. 3434	5. 3714	5. 3811

[1] Uncertainties in these pH values corresponding to the maximum deviations in the emf are the same as those listed in the last column of table 3.

The pH values may also be calculated by eq 6 expressed in the form

$$\mathrm{pH}=pK_2-\log\frac{m_{\mathrm{HAn}}}{m_{\mathrm{An}}}+\log\frac{\gamma_{\mathrm{An}}}{\gamma_{\mathrm{HAn}}}. \tag{27}$$

$\log \gamma_{\mathrm{An}}/\gamma_{\mathrm{HAn}}$ is given by $-3A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})$. The solutions measured in this investigation were made from equal molal quantities of sodium malonate and sodium acid malonate, and therefore, the $\log(m_{\mathrm{HAn}}/m_{\mathrm{An}})$ term is zero, except for the small H^+ correction (see eq 8 and footnote 7). It was found that the $\log(m_{\mathrm{HAn}}-m_{\mathrm{H}})/(m_{\mathrm{An}}+m_{\mathrm{H}})$ term could be expressed by $-1.0\times10^{-4}/\mu$ at all the temperatures. With these modifications, the pH is given by

$$\mathrm{pH}=pK_2+0.0001/\mu-3A\sqrt{\mu}/(1+Ba_i\sqrt{\mu}). \tag{28}$$

The values of pK_2 and Ba_i have been determined and A and B are given in table 2. The pH values may be calculated by this equation for solutions containing equal molal quantities of sodium acid malonate and sodium malonate of any concentration between 0.001 and 0.044 M, and for temperatures from 0° to 60° C, inclusive, with an accuracy of ±0.003 pH unit. For the convenience of the experimenter, the pH was calculated for different molalities of the malonate solutions by means of eq 28. This equation is more suitable for this purpose than eq 26. These values are given in table 10 and are shown plotted against the temperature, t° C, in figure 5.

TABLE 10.—pH *values of malonate solutions from 0° to 60° C and for rounded concentration.*[1]

[pH values of pure water at the same temperatures are included for comparison]

Rounded concentration of the solutions	μ, the ionic strength	Temperature in degrees centigrade												
		0	5	10	15	20	25	30	35	40	45	50	55	60
Moles of each solute per 1,000 g of water	*Ionic strength per 1,000 g of water*													
0.001	0.005	5.579	5.574	5.575	5.581	5.589	5.601	5.614	5.633	5.655	5.677	5.702	5.730	5.761
.002	.010	5.545	5.540	5.541	5.545	5.554	5.565	5.578	5.596	5.617	5.639	5.663	5.691	5.721
.003	.015	5.521	5.515	5.516	5.520	5.529	5.540	5.552	5.570	5.591	5.612	5.635	5.662	5.692
.004	.020	5.502	5.496	5.497	5.501	5.509	5.520	5.532	5.549	5.570	5.591	5.613	5.640	5.669
.007	.035	5.460	5.454	5.454	5.458	5.466	5.476	5.487	5.506	5.523	5.543	5.565	5.590	5.618
.010	.050	5.430	5.424	5.424	5.427	5.434	5.444	5.454	5.471	5.490	5.509	5.529	5.554	5.580
.020	.100	5.365	5.358	5.357	5.360	5.366	5.374	5.383	5.398	5.415	5.432	5.450	5.472	5.496
.030	.150	5.323	5.315	5.315	5.316	5.321	5.329	5.337	5.350	5.367	5.382	5.399	5.418	5.440
.040	.200	5.291	5.284	5.283	5.284	5.289	5.296	5.303	5.315	5.331	5.345	5.360	5.378	5.398
.044	.220	5.281	5.273	5.272	5.273	5.277	5.285	5.291	5.303	5.318	5.332	5.347	5.365	5.383
Pure water, Harned and Hamer [7]		7.469	7.365	7.267	7.173	7.084	6.998	6.916	6.840	6.768	6.698	6.631	6.569	6.509

[1] pH is defined as the negative of the common logarithm of the hydrogen-ion activity. See reference [4] for discussion of this definition. The values in this table are accurate to ±0.003 pH unit.

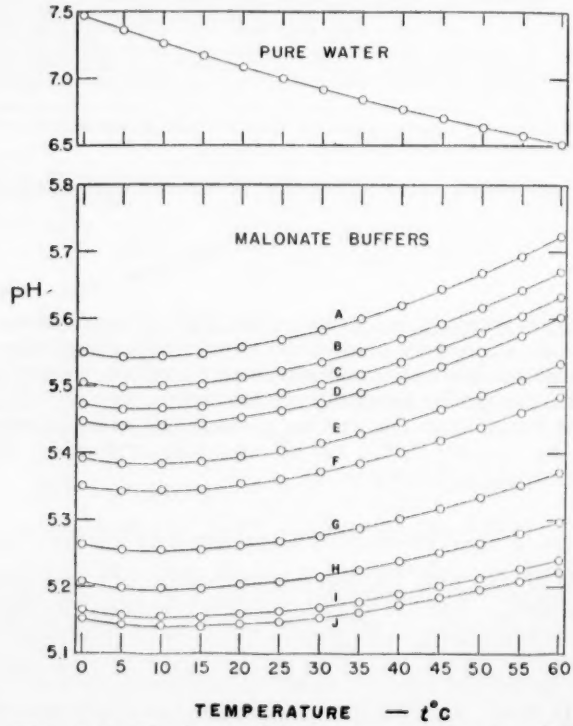

FIGURE 5.—*Plot of the* pH *values of different concentrations of malonate solutions and of pure water against the temperature*

A=0.001 *M*. *C*=0.003 *M*. *E*=0.007 *M*. *G*=0.025 *M*. *I*=0.04 *M*.
B=0.002 *M*. *D*=0.004 *M*. *F*=0.01 *M*. *H*=0.03 *M*. *J*=0.044 *M*.

The pH of a known molality of malonate solution may be conveniently obtained from the data of table 10 by interpolation. For comparison with the neutral point (pH of pure water) [7], values of the pH of pure water are given at the different temperatures in the bottom row of table 10 and are plotted in figure 5. It is to be noted that the ordinate scale for water is five times that for the solutions. Since the pH of water decreases with an increase in the temperature, the malonate solutions are very much more acidic at 0° C than at 60° C. At 0° C the pH of water minus the pH of a 0.001 *M* malonate solution is 1.919, whereas at 60° C the same difference is 0.785. In other words, at 0° C the 0.001 *M* malonate solution is 1.919 pH units on the acid side, and at 60° C it is only 0.785 pH unit on the acid side of the neutral point.

VII. THERMODYNAMIC QUANTITIES

The second ionization constant of malonic acid was determined at 13 temperatures between 0° to 60° C. It is therefore possible to determine several thermodynamic quantities. The variation of an

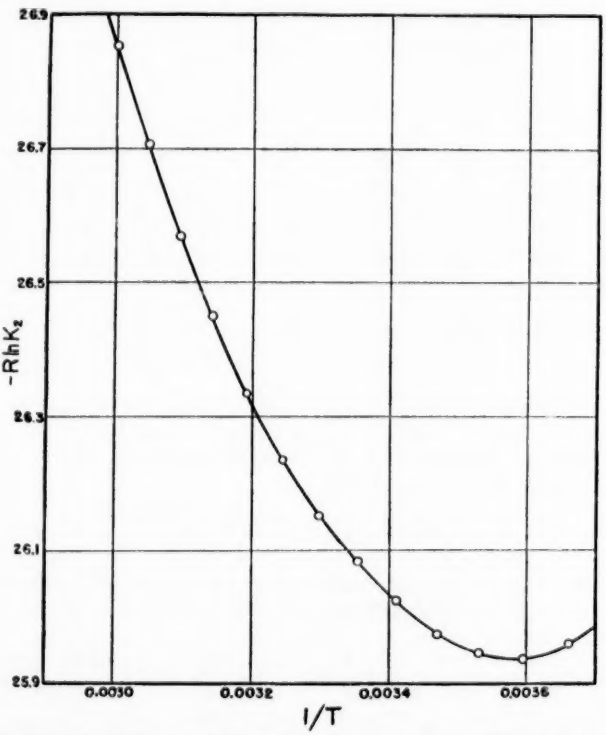

FIGURE 6.—*Plot of values of* $-R \ln K_2$ *against* $1/T$ *for a graphical evaluation of the heat of ionization of the acid malonate ion at various temperatures.*

ionization constant with temperature is given by the van't Hoff [17] isochor

$$\frac{d \ln K_2}{dT} = \frac{\Delta H_t}{RT^2}, \tag{29}$$

where ΔH_t is the heat of ionization, in this case, of the HAn− ion, and the other terms have their usual significance. To integrate this equation, it is necessary to know the relation between ΔH_t and T. This may be ascertained graphically by plotting $-R \ln K_2$ against $1/T$, figure 6, since the above equation may be written $d(-R \ln K_2)/d(1/T) = \Delta H_t$.

TABLE 11.—*Thermodynamic data from 0° to 60° C*

Temperature, t	$K_2 \times 10^8$ (observed)	ΔH_t, the heat of ionization of the acid malonate ion (obtained by a graphical method)	$K_2 \times 10^8$ (obtained from the least square equation)	ΔH_t, the heat of ionization of the acid malonate ion (obtained from the least square equation)	ΔC_p, the difference between the sum of the specific heats of the hydrogen and malonate ions and the specific heat of acid malonate ion.	$\Delta F°$, the increase in free energy for the ionization of the acid malonate ion	$\Delta S°$, the increase in entropy for the ionization of the acid malonate ion
°C		*cal*		*cal*	*cal degrees*[1]	*cal*	*cal*
0	2.140	+436	2.144	+322	−57.2	7086	−24.8
5	2.165	+79	2.157	+34	−58.1	7209	−25.8
10	2.152	−307	2.149	−259	−58.9	7342	−26.8
15	2.124	−634	2.122	−556	−59.8	7480	−27.9
20	2.076	−920	2.078	−856	−60.5	7623	−28.9
25	2.014	−1137	2.018	−1161	−61.3	7771	−30.0
30	1.948	−1424	1.946	−1469	−62.0	7921	−31.0
35	1.863	−1734	1.863	−1781	−62.7	8079	−32.0
40	1.768	−2100	1.771	−2096	−63.4	8243	−33.0
45	1.670	−2381	1.673	−2414	−64.0	8410	−34.0
50	1.575	−2695	1.570	−2736	−64.6	8580	−35.0
55	1.469	−3076	1.466	−3060	−65.1	8758	−36.0
60	1.362	−3390	1.361	−3387	−65.7	8942	−37.0

ΔH_t is obtained at each temperature by measuring the tangent to the curve. Values of ΔH_t thus obtained at each temperature are given in column 3 of table 11. The variation of ΔH_t with temperature can be expressed by the equation

$$\Delta H_t = a + bT + cT^2 + dT^3, \tag{30}$$

where a, b, c, and d are unknown constants. Substituting this equation in eq 29 and integrating, we have

$$\log K_2 = -\frac{a}{2.3026RT} + \frac{b}{R} \log T + \frac{cT}{2.3026R} + \frac{dT^2}{4.6052R} + I, \tag{31}$$

where I is the integration constant. The 13 determined values of K_2 and the corresponding temperatures were substituted in this equation. From the 13 equations, the constants were obtained by

the method of least squares. The equation for K_2 with numerical values [11] is

$$\log K_2 = -\frac{1053.08}{T} + 20.3223 \log T - 0.05838T + 0.0000236T^2 - 37.1402 \quad (32)$$

and the equation for ΔH_i, in calories, with numerical values is

$$\Delta H_i = 4818.4 + 40.3824T - 0.2671T^2 + 0.0002160T^3 \text{ cal.} \quad (33)$$

To obtain the values in calories, $R = 1.9871$ cal deg^{-1} mole^{-1}, derived by Rossini [18], was employed. This value is consistent with the constants given in table 2. Values of K_2 computed by eq 32 for the different temperatures, are given in column 4. Values of ΔH_i computed by eq 33 for the different temperatures are given in column 5. They agree fairly closely with the approximate values in column 3, obtained graphically, except at the lower temperatures, where it is difficult to read the tangent with accuracy. The sign of ΔH_i changes at about 6° C, corresponding to the maximum in the ionization constant-temperature curve.

Since $d(\Delta H_i)/dT$ equals ΔC_p [19] or $[C_p(H^+) + C_p(An^-)] - Cp(HAn^-)$, the difference between the sum of the specific heats of the H^+ and An^- ions and the specific heat of the HAn^- ion is given by

$$\Delta C_p = 40.3824 - 0.5342T + 0.0006480T^2 \text{ cal.} \quad (34)$$

Values of ΔC_p computed by this equation for the different temperatures are given in column 6 of table 11. They increase slightly with the temperature, as predicted by a semiempirical equation derived by Moelwyn-Hughes [20]. The value of ΔC_p is of the expected order of magnitude. For dissociations of molecules into ions, Pitzer [21] found from theoretical considerations that ΔC_p is about -40 cal/deg. For dissociations of ions into other ions, the value of ΔC_p should be somewhat higher owing to the increased electrostatic forces present in the latter type of dissociation.

The change in free energy, $\Delta \mathbf{F}^0$, and entropy, ΔS^0, for the ionization of the HAn^- ion are given by the equations

$$\Delta \mathbf{F}^0 = -2.3026RT \log K_2 \text{ cal.} \quad (35)$$

and

$$\Delta S^0 = \frac{\Delta H_i - \Delta \mathbf{F}^0}{T} \text{ cal.} \quad (36)$$

Values of these quantities at the different temperatures computed by the equations are given in columns 7 and 8, respectively, of table 11. The former give a measure of the extent of dissociation of the HAn^- ion. The latter are of importance in explanations of ionic dissociations [16, 20, 21], of the variation of equilibrium values and hydrogen-ion activities with temperature [22], and in interpretations of chemical reactions involving ions [23].

[11] Equations of simpler form have been proposed by Harned and Embree, J. Am. Chem. Soc. **56**, 1050 (1934) and Pitzer, J. Am. Chem. Soc. **59**, 2365 (1937) for the variation of the ionization constants of weak electrolytes with temperature. Using the forms of equations proposed by these authors and the data obtained for K_1 in this investigation, these equations are, respectively,

$$\log K_1 = -5.6675 - 0.000064(t - 4.1)^2$$

and

$$\log K_1 = 80.700 + 3626.4/T - 30 \log T.$$

Although these equations give values of K_1 at the different temperatures which agree fairly closely with the observed values, they do not reproduce the experimental data as well as eq 32. The first equation is based upon the supposition that the temperature function for ionization constants is a parabolic function. The second is based upon the assumption that ΔC_p for ionic dissociations does not vary with the temperature. Both of these assumptions represent limiting cases.

The values of ΔF^0 are obtained directly from those for K_2. The uncertainties in K_2 introduce uncertainties in the values of ΔF^0 of only 0.1 percent, or 7 to 9 calories. The values of ΔH_f and ΔC_p are subject to large error, estimated to be of the order of 100 calories in ΔH_f and 3 calories in ΔC_p. An error in ΔS^0 is determined by the errors in ΔH_f and ΔF^0 and is approximately 0.3 calorie. These uncertainties are the same at all of the temperatures. Hence, the variation of these quantities with temperature is significant. According to Pitzer [21], there are uncertainties of about 3 to 15 percent in direct calorimetric measurements of heats of ionization. In general, the heats of ionization obtained calorimetrically agree with values calculated by differentiation of emf data within this limit. Although these thermodynamic quantities are less accurate than the ionization constants from which they are derived, they are important in elucidating the state of ions in solutions and the variation with temperature of the colligative properties of electrolytes.

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HUE, SATURATION, AND LIGHTNESS OF SURFACE COLORS WITH CHROMATIC ILLUMINATION

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ABSTRACT

The visual mechanism of a normal observer is so constructed that objects keep nearly their daylight colors even when the illuminant departs markedly from average daylight. The processes by means of which the observer becomes adapted to the illuminant or discounts most of the effect of a nondaylight illuminant are complicated; they are known to be partly retinal and partly cortical. By taking into account the various fragments of both qualitative and quantitative information to be found in the literature, relations have been formulated by means of which it is possible to compute approximately the hue, saturation, and lightness (tint, value) of a surface color from the tristimulus specifications of the light reflected from the surface and of the light reflected from the background against which it is viewed. Preliminary observations of 15 surfaces under each of 5 different illuminants have demonstrated the adequacy of the formulation, and have led to an approximate evaluation of the constants appearing in it. More detailed and extensive observations have been carried out in the psychological laboratories of Bryn Mawr College, and these observations have resulted in an improved formulation.

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I. INTRODUCTION

For many years it was the view of psychologists that the chromatic-adapting power of the eye is unlimited. Constant color stimuli, they said, when acting for a long period on the retina, gradually become less effective and finally fail to produce sensations of chromatic color. When, for example, chromatically tinted glasses are continuously worn, external objects are seen sooner or later nearly in their natural or daylight colors.

This view is a correct one only when applied to moderate departures from daylight in the spectral distribution of energy of the illuminant, but it will readily be understood that there are illuminants (for example, those having all of their energy confined to a narrow wavelength region) by which there is no basis, except memory, through which all objects can possibly assume their daylight colors. For such illuminants, or for vision by an observer wearing highly selective glasses, the old view is, therefore, quite wrong [27],[1] and it becomes a matter of some interest, since we know that the eye cannot possibly detect color differences in the absence of a corresponding stimulus difference, to discover what degree of departure from daylight can be compensated for by chromatic adaptation.

The problem stated in this way was proposed by Harry Helson, Bryn Mawr College, in 1932, and in the course of planning experimental work for its solution, to be carried out jointly at the National Bureau of Standards and at Bryn Mawr College, it was found expedient to restate the problem in the following somewhat broader way: Given the radiant energy of the illuminant as a function of wavelength and the spectral apparent reflectances of the surfaces in the field of view, it is required to compute the hue, saturation, and lightness of the surface colors.

It may be noted that the latter problem includes the former and is more easily susceptible of explicit solution. Thus a slight change in illuminant changes the appearance of objects slightly, and the question of how much selectivity of illuminant can be tolerated must be answered in terms of how much change in surface color is to be tolerated. There also would be some commercial interest in the solution of this problem, if it could be done cheaply enough for a given sample; thus a frequent question to be answered by the textile salesman is, "Does this piece of goods change color in artificial light?" Another commercially important question is, "These two color samples harmonize in daylight, but do they go well together in artificial light?" The general problem stated above includes the first of these as a subproblem, and it bears importantly on the other two. The general problem, furthermore, includes that of description of chromaticity differences between large chromatic samples viewed in daylight, as by an inspector.

It is the purpose of the present paper to summarize the general principles which have been found in the literature; to present formulas for hue, saturation, and lightness which embody these principles; to describe experiments designed to test in a preliminary way the adequacy of the formulas; and to show the agreement between the formulas and preliminary experiment.

[1] Figures in brackets (sometimes followed by a page number) indicate the literature references at the end of this paper.

II. DEFINITIONS

1. PSYCHOLOGICAL TERMS

Aperture color (*Lochfarbe* [7, 48], *reduced color* [60, p. 42], *film color* [58, 60], *Flächenfarbe* [60, p. 23; 48])—color such as that experienced as filling a hole in a screen (hence, usually as a small portion of the visual field); it may be either near the plane of the screen or indefinitely far behind it; it is neither concentrated in a single plane nor spread throughout a definite volume; it is nonlocated in depth. Aperture color has the following attributes: hue, saturation, and brightness.

Volume color (*bulky color* [58], *body color* [92])—color experienced as a property of a volume or bulk.

Surface color [58] (*Oberflächenfarbe* [7, p. 419; 16; 48; 92])[2]—color experienced as a property of a surface. Surface colors are hard, resist the gaze, take the plane of the object surface, and have its texture [60, p. 23]. We deal here with three of the attributes of surface color—hue, saturation, and lightness.

Hue [87, p. 534]—that attribute of certain colors which permits them to be classed as red, yellow, green, blue, and their intermediates.

Chromatic colors [87, p. 535]—colors possessing hue.

Achromatic colors [87, p. 535]—colors not possessing hue. There is, for example, a series of achromatic aperture colors ranging between very dim and very bright, and a series of achromatic surface colors (grays) ranging between black and white.

Saturation.—The attribute of any chromatic color which determines the degree of its difference from the achromatic color most closely resembling it.

Brightness (*insistence* [48, p. 462; 60, p. 38], *Helligkeit* [7])—the attribute of any aperture color which permits it to be classed as equivalent to some member of the series of achromatic aperture colors ranging between *very dim* and *very bright*.

Lightness [37, p. 213] (*brilliance* [87, p. 534], *brightness* [60], *whiteness* [52, p. 243], *Weisslichkeit* [16, p. 612; 7])[3]—the attribute of any surface color which permits it to be classed as equivalent to some member of the series of grays ranging between *black* and *white*.

2. PSYCHOPHYSICAL TERMS

Luminous reflectance (hereinafter simply *reflectance*)—the ratio of the quantity of light reflected from a surface to that incident on it.

Luminance [37] (*brightness* [33, p. 6])—the quotient of the luminous intensity of a surface measured in a given direction by the area of this surface projected on a plane perpendicular to the direction considered.

Apparent reflectance, A, [61, p. 33]—the reflectance which a perfectly diffusing surface, under the same illuminating and viewing conditions, would have to possess in order to yield the same luminance as the surface in question. In the present work, Munsell samples

[2] Wood [92] uses the term "*color*," only in the restricted sense of chromatic color.

[3] Bocksch [7, p. 430] uses the terms *Helligkeit* and *Weisslichkeit*, in accord with our terms *brightness* and *lightness*, respectively; he makes a special point, however, of his belief that the distinction is not connected with that between surface color and aperture color, but applies to all color impressions regardless of mode of appearance. We have adopted the view given by Helmholtz [30, p. 130] as characteristic of ordinary speech; this view is supported by Fiedler's experiments [15], and also agrees with Mintz [63], who considers Fiedler's experiments to be inconclusive.

were used, and these are so nearly perfect diffusers that the illuminating and viewing conditions need not be carefully controlled, provided unidirectional illumination, with viewing at the angle of regular reflection, be avoided, as has always been done in these experiments.

Tristimulus specification [39, p. 359]—specification of the stimulus for an aperture color consisting of the amounts of three primary stimuli required to produce a color match; this specification may be computed from the spectral-energy distribution of the stimulus [23, 39], provided the visual characteristics of the observer be known. In the present work the OSA standard observer [18; 87, p. 549] was used, and the coordinate system was the uniform-chromaticity-scale (UCS) triangle [40].

Trilinear coordinates (r, g, b)—the amounts of the three primary stimuli expressed as fractions of their total. In the present work a tristimulus specification is given in the form of the relative luminance of the stimulus (proportional to the apparent reflectance of the sample since we deal here only with groups of equally illuminated samples in the same plane viewed by reflected light) combined with two of the three trilinear coordinates, it being unnecessary to give the third because, taken together, the three sum to unity by definition.

3. SPECIAL SYMBOLS

$\bar{A}$ ≡ arithmetical average apparent reflectance of the samples in the field of view.

$\bar{A}_{\log}$ ≡ logarithmic average of the same quantities.

A_0 ≡ apparent reflectance of the background against which the samples are viewed.

A_f ≡ apparent reflectance of field—the average apparent reflectance of the samples and background weighted according to proximity in past time [30, p. 268] and in space [56, p. 238] to the central part of the visual field.[4]

A' ≡ adaptation reflectance—the apparent reflectance at which a sample of trilinear coordinates equal to those of the field (r_f, g_f, b_f) appears most nearly achromatic, a function of the whole viewing situation.

I ≡ illuminance [37, p. 208] of sample plane in foot candles.

(r_0, g_0, b_0) ≡ trilinear coordinates of the illuminant.

(r_f, g_f, b_f) ≡ trilinear coordinates of the field, the parts of the field being weighted in taking an average as in the definition of A_f.

(r_n, g_n, b_n) ≡ trilinear coordinates of the stimulus for an achromatic color; these coordinates are found to be functions of the illuminant, of the particular sample fixated, and of the samples near the fixation point in the immediate past.

$D \equiv [(r-r_n)^2+(g-g_n)^2+(b-b_n)^2]^{1/2}$—distance on the UCS triangle between sample point (r,g,b) and achromatic point (r_n,g_n,b_n).

[4] Wright [94, p. 7] makes use of a parameter, the integrated light from the scene, in his discussion of adaptation; this variable is proportional to IA_f.

$D_f \equiv [(r_f-0.44)^2+(g_f-0.47)^2+(b_f-0.09)^2]^{1/2}$—distance from daylight point (0.44, 0.47, 0.09) on the UCS triangle to the field point (r_f,g_f,b_f). This distance has been found to be a fairly good index of the amount of chromatic adaptation induced by a 5-minute exposure of the observer to the field; it enters into the formulas for the trilinear coordinates of the achromatic point.

$H \equiv$ hue estimated by the observer on the following eight-point scale given to each observer as a part of his instructions: red, yellow-red, yellow, yellow-green, green, blue-green, blue, red-blue.[5] Some of the observers on their own initiative developed a 16-point hue scale formed by the introduction of intermediate hue names, such as bluish red, yellowish red, reddish yellow, and so on. Computed values of hue are given on the 8-point scale; summaries of observed hues, on the 16-point scale. The hue notation for an achromatic color is N, meaning "no hue."

$S \equiv$ saturation estimated by the observer on an 11-point scale running from zero for an achromatic color (black, gray, or white) up to 10 for the most saturated of the 15 daylight surface colors presented.

$L \equiv$ lightness estimated by the observer on an 11-point scale running from zero for black up to 10 for white, the intermediate values being used to designate a series of grays with uniform visual spacing.

$L' \equiv$ lightness expressed according to a formula derived from one deduced on theoretical ground and experimentally verified by Adams and Cobb [2], with constants adjusted to make the zero point of the scale correspond to adaptation reflectance, A', thus: $L' \equiv 10A/(A+A_f)-3.0$, from which it follows that $A'=(3/7)A_f$. As may be seen from the definition of adaptation reflectance, this choice of constants has to do with specification of the sample of trilinear coordinates (r_f,g_f,b_f) which appears most nearly achromatic, and it states that any such sample of apparent reflectance 3/7 that of the field will appear more nearly achromatic than any other such sample.

III. STATEMENT AND EXPLANATION OF FORMULAS

1. ASSUMPTIONS

The formulation is intended to apply to the colors of a group of matte, opaque surfaces viewed against a background in strong uniform illumination; it is based upon the following assumptions.

(a) COLOR MATCHING

If the aperture colors derived from two matte, opaque surfaces are identical (in hue, brightness, and saturation) and the surfaces are compared under the same illuminating and viewing conditions,

[5] This scale has also been suggested by Tschermak [91, p. 335].

it is assumed that the surface colors will be identical; and, conversely, if the aperture colors are different, the surface colors will be different. This assumption underlies all colorimetry of reflecting surfaces.

(b) HUE

It is assumed that the hue of an aperture color is determined by the direction of the straight line in the triangular mixture diagram connecting the point (r,g,b) representing the aperture color and the point (r_n,g_n,b_n) representing an achromatic aperture color of the same brightness. This is the usual interpretation of trilinear-coordinate differences; and by a further assumption, often unwarranted, that a single point can be chosen to represent achromatic colors, this assumption has led to the specification of hue by means of dominant wavelength [21; 23, p. 11; 73].

(c) SATURATION

It is assumed that the length, D, of this line indicates the saturation of the aperture color. This assumption is based upon the spacing of color stimuli yielded by the uniform-chromaticity-scale Maxwell triangle; it is regarded as a first approximation to the truth. The validity of the assumption is limited by possible failure of the UCS system to yield, as intended, substantially a uniform spacing for colors separated by small chromaticity differences, by possible failure of chromaticity differences to be arithmetically additive, and by possible important dependence of saturation upon brightness.

(d) CHROMATIC ADAPTATION

It is assumed that hue and saturation of a surface color are equal, respectively, to the hue and saturation of the aperture color derived from it for the same adaptive condition (retinal and cortical) of the observer. This assumption is a usual one among colorimetrists. If the adaptive state is not held constant, this assumption is known to be inadmissible.

(e) LIGHTNESS

It is assumed that the lightness of a surface color is a function of the apparent reflectance of the surface, A, and of the apparent reflectance of the field, A_f. (A possible slight dependence of lightness upon illuminance is neglected [7, p. 439; 86].) This assumption follows directly from the work of Adams and Cobb [2] by virtue of assumption (a); it has been stated explicitly also by Kirschmann [49, p. 363], Von Kries [56, p. 239], Bocksch [7, p. 343], A. Kohlrausch [53, p. 1501], and Kardos [44, p. 188], and is a corollary of the "approximate color constancy of visual objects" [16, 29, 31, 35, 47, 57, 60].

Further references to the principle that object color depends upon the ratios of light reflected from the various parts of the field rather than on the absolute amounts are cited by Helson [24, p. 450]. Bühler [10] stated essentially the same principle by making use of the concept, brightness of illuminated space (Luftlicht) instead of apparent reflectance of the field. Katz [48, p. 462] considered that the total brightness (insistence) of the visual field provides the crucial clue to illumination. Pikler [72] concluded from a series of experiments that light penetrating the translucent parts of the eye (iris, cornea)

and falling diffusely on the retina supplies crucial clues both to amount and to direction of the illumination relative to which lightness of visual objects is determined. Both of these views [48, 72] are consistent with this assumption (e).

2. FORMULAS

(a) HUE

Hue in accord with assumption (b) is indicated by the direction of the line on the UCS mixture diagram connecting the point representing the aperture color (r, g, b) with that representing an achromatic aperture color of the same brightness (r_n, g_n, b_n), and in accord with assumption (d) this hue applies also to the surface color corresponding to the aperture color. The direction of this line is expressed by giving its slope $(r-r_n)/(g-g_n)$, and the algebraic sign of the difference $(r-r_n)$. The relation is given symbolically in eq 1, and the table of values following it supplies the numerical data.

$$H=f[(r-r_n)/(g-g_n),\ sgn(r-r_n)] \tag{1}$$

H for $r-r_n$ greater than zero	$(r-r_n)/(g-g_n)$	H for $r-r_n$ less than zero
Red-blue	0.0 to −0.38	Green-yellow.
Red	−.38 to −.98	Green.
Yellow-red	−.98 to −2.3	Blue-green.
Yellow	−2.3 to −∞	Blue.
	∞ to 2.0	
Green-yellow	2.0 to 0.0	Red-blue.

The adjustment of these limiting values of slopes is based somewhat upon an attempt to fit our preliminary data. The angular extent assigned to each hue name is nearly a constant as would be expected on a mixture diagram of uniform chromaticity spacing, and it will be noted that the direction on the diagram assigned to red is the exact opposite of that assigned to green; similarly yellow is taken as the exact opposite of blue. It is of interest to discover how this definition of hue agrees with determinations of the stimuli for unitary and intermediate hues. Table 1 gives the wave lengths in millimicrons for the spectrum stimuli for colors of these hues found by various investigators or reported by various authorities [11, 12, 14, 80].[6] The corresponding values by eq 1 were found by taking standard ICI illuminant C [23, 39], representative of average daylight, as the stimulus for an achromatic color; that is, we have taken for this computation $r_n=0.44$ and $g_n=0.47$. It will be noted that eq 1 agrees well with experimentally found stimuli for the unitary hues, yellow, green, and blue, and for their intermediates, but specifies for the boundary between red and yellow-red a stimulus which experiment indicates actually to yield a somewhat bluer hue. This is a result of the simplifying assumption that red and green are exact opposites, and suggests that an assignment of hues without this simplifying restriction might give better agreement.

[6] For other references to this literature consult [67] and Dimmick and Hubbard [11].

TABLE 1.—*Spectrum stimuli for various hues*

Authority	Wave length in millimicrons									
	Red	Red to yellow-red	Yellow-red	Yellow-red to yellow	Yellow	Green-yellow	Green	Blue-green	Blue	Blue to red-blue
Helmholtz	687	656					527			431
Bezold		656		589	578	558	532	502	468	432
Donders					582		535		485	
Hess	PR[a]				574		495		471	
Hering	PR[a]				577		505		470	
Rood	700	621	597	588	581		527	502	473	438
Voeste					577		498		476	
Ladd-Franklin	PR[a]				576		505		470	
Von Kries					574		503			
Westphal	PR[a]				575		506		479	
Dreher					575		509		477	
Ridgway	644		598		577		520		473	
Goldytsch	PR[a]								468	
Bradley	656		608		579		514		469	
Goldmann					568		504		468	
Priest	680				583		515		475	
Brückner					578		498		471	
Schubert					574		500		467	
Maerz and Paul	644				585		521		452	
Purdy					576		504		476	
Drever	650				568		508		471	
Weld		622		597		577		492		456
Ornstein			596		575	562	515	492	475	
Terpstra		604	592	585	577	563	510	487	470	440
Verbeek		605	598	587	580	569	530	496		
Dimmick	494C[b]				582		515		475	
Experimental mean			598	589	577	566	512	495	472	439
Equation 1	521C[b]	499C[b]	601	583	575	562	521	490	476	461

[a] PR means that the indicated hue is more purple than extreme spectrum red.
[b] Dominant wavelength of the complementary is indicated by the letter C.

(b) SATURATION

In accord with assumption (c) saturation, S, is taken proportional to the length, D, of the straight line connecting the point representing the aperture color (r,g,b) with that representing an achromatic aperture color of the same brightness (r_n, g_n, b_n), and in accord with assumption (d) this saturation applies also to the surface color corresponding to the aperture color.

$$S=50D=50[(r-r_n)^2+(g-g_n)^2+(b-b_n)^2]^{1/2}. \quad (2)$$

The constant, 50, is adjusted so as to accord approximately with the scale used by the observers for expressing their estimates of saturation.

(c) ACHROMATIC POINT

It will be noted that the formulations for both hue, H, and saturation, S, (eq 1 and 2) are incomplete because the trilinear coordinates of the stimulus for an achromatic, or neutral, color (r_n, g_n, b_n) are as yet unrelated to the observing situation. By means of these trilinear coordinates, the chromatic adaptation (retinal and cortical) of the observer is to be defined. When a daylight-adapted observer enters a room illuminated by light differing chromatically from daylight to an important extent, a rapid chromatic adaptation takes place

which is fairly complete in about 5 minutes. A large part of this chromatic adaptation may occur immediately; that is, the observer may immediately react to the surfaces as if they were illuminated by chromatic light, and there is an immediate reverse change either if the observer begins to react again to the surfaces as if illuminated by daylight, or if the samples lose their surface character and are seen as aperture colors [60, p. 10].[7] This fluctuation occurs with a facility and time character roughly equal to those with which ambiguous pictures (such as the reversible staircase) fluctuate; and, indeed, the situation with which the observer is presented is more than ambiguous, because there are usually not two but many equally valid responses possible depending on the allocation of the chromatic component of the aperture color partly to the surface color and partly to illumination color [60, p. 39] in various proportions.[8] The instantaneous changes are usually considered to be cortical [7, p. 433; 10, p. 115; 35]; some have considered the initial rapid change also to be wholly cortical, but there is considerable evidence for instantaneous retinal adaptation of electrical origin [82, 94, 95]; so it is probable that neural activity, both retinal and cortical, is involved in an essential way [4, 55, 64, p. 46]. The slower progressive changes usually coming to completion in about 5 minutes are thought to be retinal. During this time interval, the values of the trilinear coordinates (r_n, g_n, b_n) specifying the chromatic adaptation of the observer undergo corresponding changes, and no attempt has been made in the present work to separate the retinal from the cortical components, or to trace quantitatively either the course of retinal adaptation in time, as has been done by Wright [93], or its definition in terms of these trilinear coordinates (r_n, g_n, b_n). During the period following that of rapid change, an approach to equilibrium often occurs, and it has been found successful to a considerable degree to define this equilibrium state by means of eq 3, as follows:

$$\left.\begin{aligned} r_n &= r_f - D_f[0.1\ L'(r_f - 0.360) - 0.018\ b_f A_f (L')^2 \log_{10} 2000I] \\ g_n &= g_f - D_f[0.1\ L'(g_f - 0.300) - 0.030]. \end{aligned}\right\} \quad (3)$$

Formula 3 embodies several ideas that have been widely accepted for many years. When, as was the case in our preliminary experiments, the visual field is filled with objects which, taken together, are spectrally nonselective, so that we may write $r_f = r_0$ and $g_f = g_0$, these formulas could yield strict "color constancy of visual objects" [31] only by the first terms taken alone; the longer second terms (commencing with D_f) may therefore be considered as correction terms indicating necessary departure from strict "color constancy." These correction terms describe variations of the achromatic point (r_n, g_n, b_n)

[7] Many observers can shift colors from the surface mode of appearance to the aperture mode at will [60, p. 45]. Thus A. Gelb [16, p. 599] writes, "In this respect it must be noted particularly that under certain conditions *even without the reduction screen* the dark gray paper near the window and the white wall further back can be seen in the way that corresponds with the relations between the physical stimuli. (The same thing holds for other examples.) Of course, to do this requires a characteristic inhibition, more foreign to reality, which we may designate as the 'attitude of pure optics'; we must consider the color of the paper and that of the wall 'critically' (Katz)—contrary to the natural objective way, that is, as Köhler has opportunely remarked, we must detach ourselves from the objectivity of the surface of the objects and degrade them to a kind of light area. Many people achieve this attitude relatively easily, particularly those who have an aptitude for painting; indeed they must use a dark gray pigment to represent a weakly illuminated white (such as the white-painted wall far back from the window). Whoever achieves the mode of seeing referred to, sees, to be sure, the color of the paper and that of the wall in accord with the relative illuminations; however, he does not see 'true objects' (paper, wall) of particular definite colors in different illuminations, but 'color areas' . . ."

[8] For example, a surface in red light may appear sometimes red and sometimes white or pink according to Bocksch [7, p. 371].

from the field point (r_f,g_f,b_f). Such variations were known as early as 1860, for we read in Helmholtz [30, p. 274], "When a particular color is made dominant in the visual field, a paler shade of the same hue will look white to us, and real white will seem to be the complementary color. Thus the idea of what we mean by white is altered in this case." This is an approximate statement of the facts and would lead to formulas for the achromatic point of the form

$$\left.\begin{aligned} r_n &= r_f - k(r_f - r_w) \\ g_n &= g_f - k(g_f - g_w) \end{aligned}\right\}, \tag{3a}$$

where (r_w,g_w,b_w) are trilinear coordinates of the original "white" point. Formula 3a describes excursions of the achromatic point along the straight line connecting the field point with the original "white" point, depending on the value of the constant, k, indicating degree of departure from adaptation to the field. These formulas also cover a conclusion by Kravkov [54] concerning the direction of surface-color transformation from a chromatic illuminant. Equation 3 includes four separate elaborations or corrections of this idea.

The first elaboration is the introduction of the term L', which extends eq 3a to light and dark parts of the visual field according to the principle that nonselective samples of apparent reflectance considerably greater than the adaptation reflectance, A', take the hue of the illuminant, while those of apparent reflectance considerably less take the hue of the after-image complementary [24]. Helmholtz was familiar with these facts also; he said [30, p. 275], "When we look steadily through a red glass, soon all perfectly dark objects appear to be a vivid green. Thus, alongside the red its complementary color becomes visible, . . ." This account accords with our results, except that the after-image complementary is greenish blue instead of green. Troland [88] and Karwoski [45] also called attention to the same phenomenon for stationary fixation point under the name "dimming effect." Hering [13] had previously proposed the dimming technique as a means of differentiating achromatic aperture colors from those of low saturation.

The discrepancy between mixture complementary and after-image complementary gives rise to the second elaboration of eq 3a. The after-image complementary departs from the mixture complementary by having more red-blue [19; 90; 91, p. 474; 93; 65][9]; this departure is indicated first by the introduction of the term, $0.030\,D_f$, as an addition to g_n, second by the use of the trilinear coordinates (0.360, 0.300) different from those (r_w,g_w) suggested by eq 3a, and third by the $(L')^2$ term in the expression for r_n. It was found necessary to introduce all three changes to obtain agreement with our preliminary data.

A third elaboration was introduced to take account of the greater prevalence of chromatic after-image or adaptation effects for certain regions of the Maxwell triangle. Thus for the field point (r_f,g_f,b_f) near the daylight point (0.44, 0.47, 0.09), no chromatic responses not accounted for by the spectral selectivity of the samples were found;

[9] Tschermak [91, p. 474] gives eight other references.

hence, the term D_f was introduced. Failure of Dittler and Satake [13, p. 245] to find a stimulus for an achromatic color which would also yield on dimming an achromatic color suggests that the correct term is $(k+D_f)$; but our preliminary experiments did not seem to require the introduction of the small constant term, k.

It is of interest to note that Katz [47; 60, p. 37] originally took "normal illumination" to be that found "in the open air under a lightly clouded sky," which has closely the trilinear coordinates (0.44, 0.47, 0.09) relative to which D_f is defined.

The fourth elaboration has to do with an intensification of afterimage effects for the blue illuminant for high illuminances, I, and for high field reflectances, A_f. For this reason the term involving the product, $b_f A_f \log_{10} 2000\, I$, was introduced. This term depends upon information obtained from the extensive data collected by Helson and Jeffers [25, 26] which were made available in advance of their publication through the courtesy of Professor Helson. Our preliminary results refer to a single illuminance for each chromatic illuminant; so they do not afford a check upon this term, although they are consistent with it. If this term were omitted, eq 3 would define two field points on the Maxwell triangle for which hue and saturation are independent of lightness, L', instead of one field point (0.44, 0.47, 0.09). The second field point (0.36, 0.30, 0.34) was tentatively named the "blue, hueless point;" blue, because it undoubtedly refers to a blue illuminant, and hueless, because the equations suggested that a nonselective sample under an illuminant plotting at that point would generally, independent of lightness, appear gray or hueless. Attempts by Helson to set up a "blue, hueless" illuminant, however, were unsuccessful; the illuminants tried gave afterimages of feeble rather than zero chromatic component, and led to the $(L')^2$ term in eq 3. This term adds a component of greenish blue to the computed color both for bright and for dim parts of the visual field, the amount of which is proportional to $D_f b_f A_f$. The effect of this term combined with the term $0.030\, D_f$ in the expression for g_n is to make surface colors by computation tend toward red-blue for bright visual fields having D_f and b_f greater than zero.

Equation 3 is therefore consistent with many of the data in the literature of visual psychophysics, with the preliminary data to be discussed presently, and with recent experimental data by Helson particularly adapted for testing out certain aspects of the formulation. But there is no basis for believing that it is the only formula meeting these conditions.

(d) LIGHTNESS

Lightness in accord with assumption (e) is computed from the apparent reflectance, A, of the surface in question and from the apparent reflectance of the field, A_f. The Adams and Cobb [2] formula has already been used to define lightness, L', and this is also used for comparison with estimates of our observers after adjustment of the end points of the scale to make zero correspond to the lower limit of apparent reflectance shown by our samples ($A=0.03$) and to make 10 correspond to the upper limit ($A=1.00$); these choices were made in order to give agreement with our observers' estimates of

lightness near the ends of the lightness scale, black and white, and they lead to the following formula:

$$L=10(L'-L'_{A=0.03})/(L'_{A=1.00}-L'_{A=0.03}). \quad (4)$$

By substituting the definition of L' in eq 4, the following explicit function of A and A_f, quoted by Helson [24, p. 453], is found:

$$L=\frac{10(A-0.03)\ (A_f+1.00)}{(1.00-0.03)\ (A_f+A)}. \quad (4a)$$

(e) OBSERVING SITUATIONS

Case 1.—If an observer adapted to daylight enters an enclosure filled with an illumination chromatically different from daylight, and is confronted with an array of samples, with instructions to report immediately on the aperture color derived from one of them, we should expect to compute the resulting estimates of hue and saturation from eq 1 and 2, in which the trilinear coordinates of the achromatic point (r_n, g_n, b_n) would be set equal to those for the daylight point (0.44, 0.47, 0.09). This is the classical case for which hue can be correlated with dominant wavelength computed relative to the daylight point; the observing situation to which it applies is often very transient, sometimes lasting less than a second.

Case 2.—If, however, the observer is instructed to report on a surface color as objectively as possible (that is, with an attempt to discount the illuminant color), his report, except for minor effects from simultaneous contrast, should be expected to correspond with eq 1, 2, and 3, with trilinear coordinates of the achromatic point (r_n, g_n, b_n) taken equal to those for the illuminant point (r_0, g_0, b_0). The period during which such computed hues and saturations could apply would be limited to a few seconds (5 or 10), this duration being usually too small for the development of a chromatic adaptation sufficient to influence the surface color by projection of a negative after-image of the background upon the sample [30, p. 267]. To set the achromatic point equal to the illuminant point was suggested by Priest [74], who said in support of his suggestion, "It is a well-known and significant fact that nonselective diffusely reflecting surfaces are constantly *perceived* as 'white' (or 'gray') for a wide range of variation in the spectral distribution of the illuminant." This suggestion is also implied and justified by Koffka's concept of "shift of level" [51; 52, p. 255]. By arguments based upon chromatic adaptation, which refer to field point instead of illuminant point, a similar suggestion was put forward for longer durations by Ives in 1912 [34], and by Noteboom [71] and Ströble [85] in 1934. This suggestion, intended to apply to extended durations, is allied to the "coefficient law" formulated by Von Kries [30, p. 441; 56, p. 211], and was also implied by Troland [89, p. 182] when he wrote, "* * * it appears that this process (chromatic adaptation) changes the proportions of ordinates between the color-mixture elementaries, so that we must compute the colors on the basis of a distorted triangle."

Case 3.—If the observer remains in the enclosure looking at the array of samples against a background for 5 minutes or more, and if he is asked to report upon the surface color of a sample from its appear-

ance by momentary fixation, his report should be expected to correspond with those for the achromatic point defined by eq 3, in which the apparent reflectance of the field, A_f, is an average of the apparent reflectances of the samples and of the background, A_0, against which the samples are viewed. Since about half of the sample plane in our preliminary experiments was covered with samples, the other half consisting of the background, we have computed A_f representative of observation by momentary fixation preceded by a moving fixation point as follows:

$$A_f=(A_0+\overline{A})/2. \tag{5a}$$

This formulation applies only to momentary observation preceded by a fast-moving fixation point, because the surface color by eq 1, 2, 3, and 4 is identified with the hue, saturation, and lightness produced by projecting an after-image of the field as a whole (A_f, r_f, g_f, b_f) upon the sample. The observer can easily tell when he fails to comply with these conditions. If his fixation point pauses too long preceding fixation of the sample, he gets a patterned after-image, which by its pattern seems not to belong to the sample [30, p. 269]. If he fixates the sample, itself, too long, the after-image of the field as a whole will die away causing him to change his report; or, perhaps, to note that the first report applies only to the edges of the sample where an after-image of the background has been renewed by small movements of the fixation point within the sample [30, pp. 268, 273]. The color of the center of the sample is dealt with in case 4.

Case 4.—If in case 3 the observer fixates the sample to be reported upon for more than a second or two,[10] we should expect the apparent reflectance, A, of the sample itself to enter into the average for A_f; the longer the fixation, the greater the weight, n, of A, thus,

$$A_f=(nA+A_0+\overline{A})/(n+2). \tag{5}$$

It will be noted, of course, that eq 5a is the special case of eq 5 obtained by setting $n=0$. The special case corresponding to fixation of the sample, until equilibrium is reached, will be found by setting $n=\infty$; this gives

$$A_f=A. \tag{5b}$$

From the definition of L', it will be seen that eq 5b leads, except for $A=0$, to a value of L' constant at $+2$, which, in turn, through eq 1, 2, and 3, leads to hues and saturations characteristic of bright parts of the visual field, that is, to hues and saturations in accord with the principle, discussed by Helson [24], that bright parts arising from nonselective samples take the hue of the illuminant. This result accords with experiments by Helson and Judd [27] on the appearance of a uniform visual field after prolonged adaptation to it; only in a few exceptional cases did the original hue disappear after minutes-long adaptation, and then only in the sense of appearing and disappearing in rhythmic alternation.

Although our observers were instructed to report upon the appearance of the samples by momentary fixation (case 3), it is of interest

[10] It seems likely from Newhall's work [69] that blinkless fixation for as little as 5 seconds can introduce significant change.

to attempt a prediction of the colors which they would obtain by using longer than momentary fixation contrary to instructions; in this way there may be discovered an explanation for some of the individual variations which cannot be explained by the variable allocation of chromatic component between the surface and the illuminant. For this purpose a value of n between zero and infinity must be chosen, and we have taken, from a preliminary examination of Helson's data as well as our own, n equal to 2, which gives

$$A_f=(2A+A_0+\overline{A})/4. \tag{5c}$$

It may not be immediately apparent that eq 5c favors the appearance of the illuminant hue more than eq 5a; however, adaptation reflectance, A', by eq 5a, is $(3/14)(A_0+\overline{A})$, as may be seen from the definition of L', but by eq 5c it is only $(3/22)(A_0+\overline{A})$; so eq 5c gives a considerably larger range of apparent reflectance for which a nonselective sample would take on the illuminant hue.

TABLE 2.—*Adaptation reflectance, A'*

	Expression for A'	Adaptation reflectance for $\overline{A}=0.33$, $\overline{A}_{log}=0.24$			
		$A_0=0.03$	$A_0=0.10$	$A_0=0.23$	$A_0=0.60$
Present preliminary experiment, selective samples.	$0.6(A_0\overline{A}_{log})^{1/2}$	0.051	0.093	0.141	0.263
	$(3/14)(A_0+\overline{A})$ [eq 5a]	.077	.092	.120	.242
Helson and Jeffers [26], selective samples.	$0.32(A_0\overline{A}_{log})^{1/2}$	.027	.050	.075	.140
	$(3/22)(A_0+\overline{A})$ [eq 5c]	.049	.059	.076	.154
Helson [24], nonselective samples.	$0.8(A_0^3\overline{A}_{log})^{1/4}$	.041	.100	.186	.474
	$(5/28)(3A_0+\overline{A})$	.075	.112	.182	.467

Table 2 shows a comparison between values of adaptation reflectance, A', computed by eq 5a and 5c, and those found from an examination (a) of our preliminary experimental results represented by the formula $0.6(A_0\overline{A}_{log})^{1/2}$, and (b) of the experimental results of Helson and Jeffers [26] on selective samples represented by the formula $0.32(A_0\overline{A}_{log})^{1/2}$. It will be noted from table 2 that eq 5a yields values of A' in good agreement with the logarithmic formula previously found for our preliminary experimental results; the logarithmic formula found by Helson and Jeffers for adaptation reflectance in their experiments with the same selective samples does not, however, agree with eq 5a, but it agrees well with eq 5c. This suggests that Helson's observers used longer fixation of sample than ours did. Values of adaptation reflectance found by Helson from his results with nonselective samples [24] represented by the formula $0.8(A_0^3\overline{A}_{log})^{1/4}$ are also given; these values are seen not to agree with either of the other two sets. Since, however, the background was more effective in

determining adaptation reflectance in these experiments, as is evidenced by the weight 3 given to A_0 in the logarithmic mean, these values have been compared with $(5/28)(3A_0+\bar{A})$ and found to agree fairly well.[11] The previous view [41] that calculations of apparent reflectance of the field, A_f, should be made by logarithmic mean [24] has therefore been given up in the present treatment. The arithmetical mean is not only adequate, simpler, and applicable to fields involving completely dark areas ($A=0$), but it has also yielded improved agreement with lightness estimates of our observers, as will be seen presently. The improved values of adaptation reflectance which have resulted chiefly from Helson's work [24] have been found to permit the elimination of a factor $(1+10\ b_f)$ previously considered to be a necessary part of eq 3 [41].

These four cases describing different observing situations have been worked out for the samples used in our preliminary experiments, and it is believed that other cases are of little interest at present. One factor, however, in the observing situation which has been shown, under some circumstances, to be the controlling one has yet to be mentioned. This is the presence in the visual field of objects whose daylight colors are known to the observer. It has been shown [3] that the observer may report the "memory color" of the object instead of the color reported by an observer who is ignorant of the daylight color. No precautions were taken in our work to prevent the observers from learning the daylight colors of the samples or to prevent the subsequent identification of the samples by the shapes, which were fairly distinctive; but none of our preliminary results seem to be spurious from this cause. Although memory color may be an important factor influencing the color perceptions of an observer distracted by another task, we found that the surface color for our observing conditions was generated from the situation itself with ambiguities so limited as to exclude responses appropriate to memory color except for a few sample-illuminant-background combinations which chanced by the formulation also to yield approximately the daylight color.

IV. ILLUMINANTS AND SAMPLES USED

The samples used in the preliminary experiments were 15 Munsell papers whose apparent reflectances relative to magnesium oxide as functions of wavelength had been determined in 1926 for another purpose.[12] These samples were also used by Helson and Jeffers [25, 26]. Some measurements of apparent reflectance were made on each sample for nearly diffuse illumination and normal viewing, and some were made for 45-degree unidirectional illumination and normal viewing. There was no certain difference between the values obtained in these two ways, and the values adopted are based on both; they are given in table 3.

[11] The constant, 5/28, corresponds to a redefinition of L' as $10A/(A+A_f)-4.2$. Why these data require this minor change in definition of L' is not known.

[12] NBS test No. 46045. The samples are identified by Munsell notation in accord with the original Atlas of the Munsell Color System [66].

TABLE 3.—*Spectral apparent reflectances for the 15 Munsell samples studied*

Wavelength	R 3/7	R 5/10	R 7/6	YR 4/5	Y 5/7	Y 7/8	G 3/4	G 5/7	G 7/7	B 3/5	B 5/6	B 7/4	P 3/6	P 5/6	PB 7/4
mμ															
380	0.0680	0.084	0.120	0.0502	0.0630	0.0678	0.0684	0.0457	0.080	0.090	0.123	0.098	0.115	0.102	0.113
90	.0672	.123	.341	.0504	.0651	.0710	.0685	.0481	.153	.185	.351	.400	.247	.350	.420
400	.0655	.123	.364	.0507	.0655	.0729	.0687	.0521	.200	.188	.357	.515	.262	.387	.519
10	.0630	.122	.368	.0512	.0655	.0742	.0692	.0597	.232	.187	.355	.558	.264	.405	.551
20	.0601	.120	.366	.0517	.0654	.0754	.0700	.0708	.261	.187	.355	.579	.257	.410	.574
30	.0567	.118	.363	.0524	.0654	.0765	.0711	.0895	.292	.194	.367	.597	.244	.403	.596
40	.0534	.115	.359	.0532	.0655	.0779	.0730	.119	.325	.214	.407	.615	.226	.390	.619
450	.0503	.113	.353	.0542	.0659	.0795	.0770	.152	.362	.235	.455	.633	.207	.371	.637
60	.0476	.111	.346	.0553	.0665	.0819	.0825	.191	.409	.249	.504	.652	.186	.352	.645
70	.0454	.107	.340	.0566	.0675	.0855	.0890	.233	.463	.253	.545	.666	.167	.331	.641
80	.0437	.104	.334	.0582	.0695	.0922	.0955	.278	.517	.248	.555	.675	.149	.310	.630
90	.0426	.101	.329	.0602	.0734	.105	.101	.325	.562	.235	.535	.674	.131	.289	.617
500	.0420	.0980	.328	.0631	.0803	.141	.106	.371	.600	.215	.497	.665	.115	.269	.600
10	.0417	.0955	.330	.0673	.100	.210	.111	.413	.627	.194	.450	.649	.104	.252	.573
20	.0419	.0948	.332	.0741	.148	.307	.114	.435	.639	.169	.401	.628	.0965	.239	.537
30	.0429	.0963	.338	.0850	.206	.424	.114	.432	.632	.145	.351	.604	.0935	.231	.500
40	.0448	.100	.347	.100	.250	.523	.110	.399	.610	.123	.306	.578	.0925	.228	.470
550	.0482	.106	.359	.127	.276	.570	.105	.355	.582	.105	.269	.552	.0934	.228	.448
60	.0545	.118	.377	.158	.289	.588	.0985	.307	.550	.0920	.238	.527	.0959	.231	.430
70	.0648	.143	.410	.188	.294	.595	.0908	.256	.512	.0832	.212	.502	.100	.235	.415
80	.0818	.200	.482	.219	.296	.596	.0839	.212	.475	.0769	.195	.480	.107	.241	.402
90	.114	.293	.599	.245	.295	.594	.0780	.176	.442	.0721	.184	.460	.114	.250	.395
600	.153	.433	.688	.265	.292	.591	.0734	.148	.414	.0684	.175	.440	.119	.264	.390
10	.191	.563	.741	.276	.288	.588	.0702	.127	.390	.0657	.169	.422	.124	.279	.389
20	.221	.639	.763	.285	.283	.585	.0684	.111	.370	.0641	.164	.406	.129	.297	.391
30	.244	.680	.774	.290	.277	.581	.0677	.0992	.353	.0635	.161	.394	.134	.315	.398
40	.263	.701	.778	.295	.272	.578	.0685	.0895	.338	.0634	.159	.384	.140	.336	.408
650	.280	.712	.782	.298	.269	.575	.0705	.0832	.325	.0637	.157	.377	.148	.359	.423
60	.294	.721	.786	.302	.268	.573	.0737	.0789	.315	.0645	.158	.373	.158	.383	.441
70	.305	.728	.790	.305	.268	.575	.0777	.0755	.306	.0657	.160	.370	.170	.408	.462
80	.321	.735	.793	.308	.270	.575	.0824	.0730	.299	.0673	.165	.370	.190	.433	.487
90	.342	.743	.797	.312	.274	.578	.0871	.0713	.294	.0692	.175	.371	.218	.459	.515
700	.368	.750	.800	.315	.280	.582	.0918	.0702	.289	.0712	.191	.374	.253	.484	.546
10	.398	.756	.803	.317	.287	.586	.0965	.0695	.285	.0735	.214	.379	.296	.509	.580
20	.429	.763	.806	.320	.296	.593	.101	.0692	.283	.0762	.247	.384	.351	.529	.620

The illuminants used were natural daylight from a south window and four chromatic illuminants (red, yellow, green, blue) obtained by illuminating the samples with a 500-watt, gas-filled lamp and viewing them through one or another of four Corning glass filters whose spectral transmissions were determined chiefly on a photoelectric spectrophotometer [17] and are given in table 4. A few of the lowest transmissions were checked by means of the König-Martens visual spectrophotometer [62]. The natural daylight supplied an illuminance of about 50 footcandles; the 500-watt lamp, about 700.

TABLE 4.—*Spectral transmissions of the viewing filters*

Wavelength	Lantern red	Lantern yellow	Sextant green	Lantern blue
mμ				
380		0.0002		0.15
90		.0002		.28
400		.0002	<0.0005	.365
10	*<0.001	.0002		.400
20		.0002	.0002	.404
30		.0002	.0003	.400
40	<.00005	.0002	.0004	.384
450		.0002	.0010	.360
60	<.00002	.0003	.0022	.318
70		.0003	.0056	.240
80	<.00002	.0004	.0133	.143
90		.0005	.0280	.070
500	<.00002	.0007	.0580	.033
10		.0011	.0916	.0100
20	<.000005	.0017	.109	.0038
30		.0030	.112	.0017
40	<.000005	.0055	.098	.0010
550		.025	.070	.0013
60	<.000005	.278	.042	.0021
70		.475	.0228	.0014
80	<.00001	.539	.0104	.0004
90	<.00001	.580	.0045	.0001
600	<.00005	.608	.0017	.0001
10	.0002	.630	.0004	.0001
20	.025	.646	<.0002	.0001
30	.273	.660		
40	.548	.668	<.0002	<.0001
650	.645	.672	<.0001	
60	.681	.675		<.0001
70	.699	.676	<.0001	
80	.707	.677		.0001
90	.710	.678	<.0001	.0006
700	.713	.674	<.0001	.0015
10	.714	.669		.0027
20	.714	.656	<.00005	.0025
30	.714	.650		.0023
40	.714	.641	<.00005	.0022
750	.712	.636		.0020
760	.711	.629	<.00005	.0018

* Numbers preceded by the "less-than", <, sign indicate spectral transmissions greater than those possessed by the respective filters.

The tristimulus specifications of the light reflected by each of the 15 samples when it is illuminated in turn by each of the 5 illuminants were computed from the data of tables 3 and 4. Standard ICI illuminant *A* [23, 39] was used in these computations as representative of the 500-watt lamp; and Abbot-Priest sunlight [38, p. 525] was used as representative of natural south daylight. The OSA observer and coordinate system [18; 87, p. 549] was used for the first computation of tristimulus specifications, and these were later transferred to the uniform-chromaticity-scale system [40]. Table 5 gives two (r and g) of the trilinear coordinates on this system; the third may be found, if desired, as $b=1-r-g$.[13] Figure 1 shows the uniform-chromaticity-scale triangle on which have been plotted points representing (except for the red illuminant) each of the 15 samples under each

[13] Computations of trilinear coordinates, r, g, b, and of apparent reflectance, A, for these 75 illuminant-sample combinations were carried out by Mabel E. Brown.

of the 5 illuminants. The illuminant point is indicated by a square. The samples under sunlight illumination are shown by circles, with large circles for the five samples having the most saturated colors of the five Munsell hues, red, yellow, green, blue, and purple. For the strongly chromatic illuminants, the samples are shown by crosses, with large crosses for the same five samples shown by large circles for sunlight illumination. For the red illuminant, only the green (G) and the purple (P) samples are shown; points for the other samples fall on the straight line connecting these two points, and, for the sake of clarity, crosses to indicate them have been omitted. It will be noted that points representing the samples for other illuminants than red do not cluster as closely about the illuminant point. The small cluster of points for the red illuminant is related to the greater selectivity of the red filter (see table 4).

TABLE 5.—*Trilinear coordinates (r, g) of the light reflected from each sample and the apparent reflectances (A) of the samples for each of the five illuminants used*

Sample	Abbot-Priest sunlight			Red illuminant			Yellow illuminant			Green illuminant			Blue illuminant		
	r	*g*	*A*	*r*	*g*	*A*	*r*	*g*	*A*	*r*	*g*	*A*	*r*	*g*	*A*
MgO	0.458	0.458	1.000	0.958	0.042	1.000	0.705	0.295	1.000	0.372	0.613	1.000	0.237	0.351	1.000
R 3/7	.606	.342	0.087	.961	.039	0.276	.792	.208	0.151	.390	.597	0.049	.243	.338	0.048
R 5/10	.628	.327	.221	.959	.041	.706	.796	.204	.404	.391	.595	.110	.241	.344	.110
R 7/6	.527	.408	.459	.958	.042	.781	.744	.255	.618	.380	.606	.357	.240	.347	.346
YR 4/5	.574	.394	.163	.959	.041	.297	.735	.265	.246	.401	.589	.110	.248	.365	.099
Y 5/7	.525	.448	.241	.957	.043	.272	.700	.299	.288	.393	.598	.221	.254	.373	.097
Y 7/8	.532	.449	.490	.958	.042	.577	.703	.296	.588	.393	.598	.455	.265	.398	.158
G 3/4	.437	.490	.094	.961	.039	.072	.686	.313	.078	.367	.619	.107	.236	.369	.093
G 5/7	.407	.539	.285	.953	.047	.087	.637	.362	.171	.362	.624	.377	.237	.413	.267
G 7/7	.439	.497	.522	.956	.044	.329	.677	.322	.428	.367	.619	.596	.237	.384	.499
B 3/5	.374	.485	.114	.958	.042	.064	.685	.314	.072	.351	.629	.133	.232	.353	.217
B 5/6	.386	.491	.277	.959	.041	.161	.684	.315	.185	.354	.627	.324	.232	.363	.472
B 7/4	.427	.478	.531	.957	.043	.381	.690	.309	.445	.365	.619	.581	.236	.356	.642
P 3/6	.440	.423	.108	.962	.038	.153	.730	.270	.119	.370	.612	.097	.237	.325	.153
P 5/6	.456	.434	.253	.961	.039	.359	.731	.269	.273	.370	.614	.235	.236	.337	.310
PB 7/4	.428	.467	.458	.960	.040	.428	.704	.294	.405	.364	.619	.485	.236	.350	.600

Table 5 also gives the apparent reflectance of each sample computed for each of the five illuminants. The three numbers (A, r, g) serve to specify the beam reflected from the sample toward the observer relative to that which would be reflected from a surface of magnesium oxide, which was the reflectance standard used in the spectrophotometric work [68].

V. EXPERIMENTAL METHOD

The observer was shown the samples (irregularly shaped papers of about 1 in.^{2}) spread out in disarray on one of two large cardboards (either a light one, A_0=0.80, which appeared white in daylight, or a dark one, A_0=0.10, which appeared dark gray). He was asked to arrange them in order of lightness, placing the lightest at the top and the darkest at the bottom. After this task had been done, he was asked to estimate the lightness on a scale of 10 equal visual steps such that white would have lightness, L=10, and black would have lightness, L=0. These estimates were recorded. Then he was asked to arrange the samples in order of saturation, placing the one having the

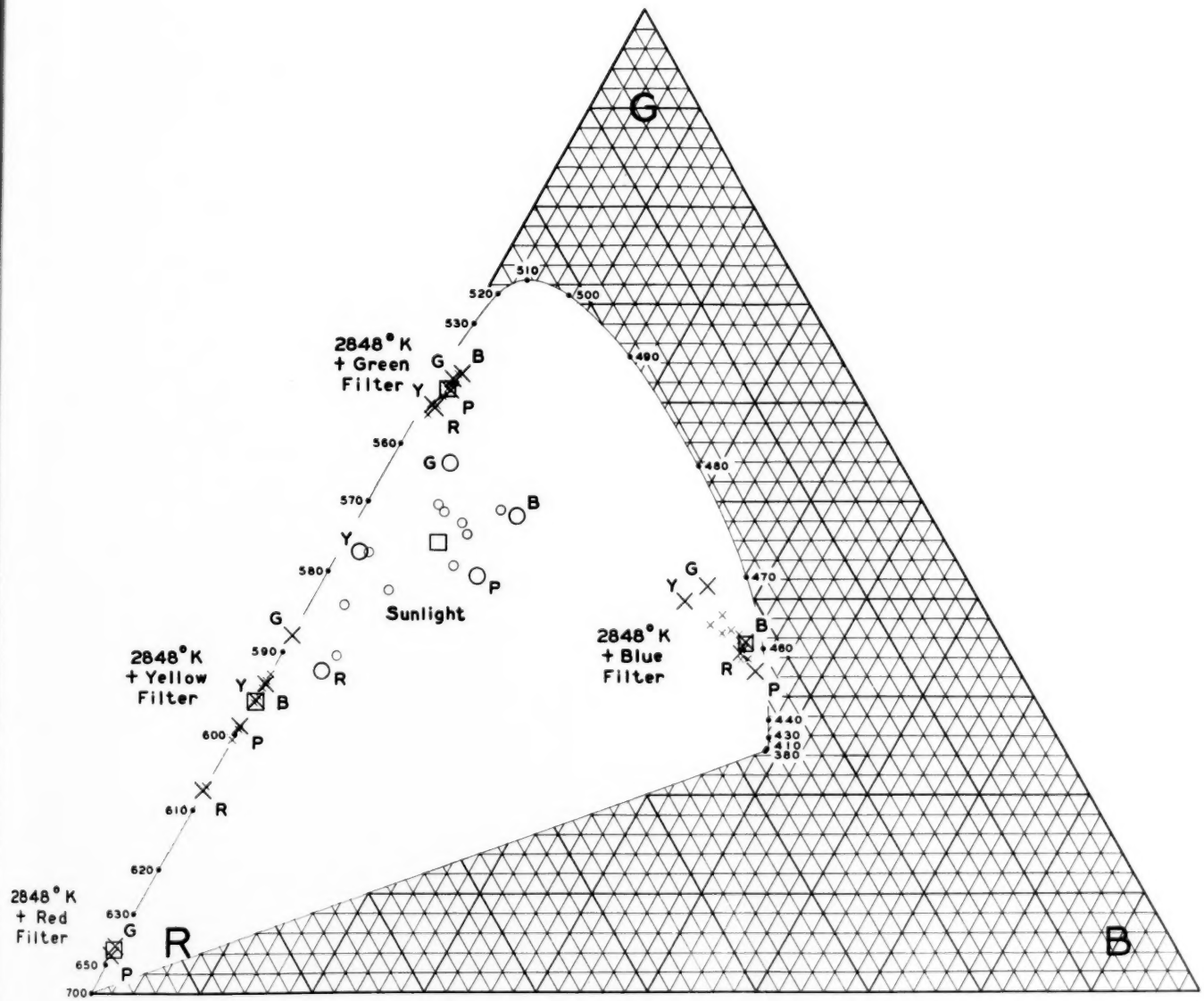

FIGURE 1.—*The 75 illuminant-sample combinations represented on the uniform-chromaticity-scale Maxwell triangle.*

The samples with Abbot-Priest sunlight as the illuminant are shown by circles; those for the four strongly selective illuminants (red, yellow, green, blue) are shown by crosses. The illuminants are indicated by squares.

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most saturated (strongest) color first and the one most closely resembling an achromatic color last. After this task had been done, he was asked to estimate the saturation on a scale of 10 equal visual steps, such that the strongest daylight color produced by any of the 15 samples would be assigned the saturation, $S=10$, and such that an achromatic color would be given a saturation, $S=0$. Then he was asked to name the hue of the sample on the eight-point hue scale; see definition of H, section II–3. These saturation and hue estimates were also recorded. If, as was frequently the case, the observer was not satisfied with one of the 8 or 11 answers suggested by these 8- and 11-point scales, his estimate was recorded on a more finely divided scale. This procedure was carried out for each observer for all five illuminants, and for each of the two backgrounds. In his manipulation of the samples, the observer was not permitted to place the samples next to one another except in forming estimates of lightness; for hue and saturation estimates the samples were kept about one-half inch apart. Furthermore, the observer was requested to avoid fixating any one sample very long at a time; he was encouraged to look rapidly from one sample to another in order to avoid as much as possible the influence of any one sample on estimates of the color of another.

Although estimates of this sort have sometimes been criticized as meaningless (see, for example, Smith [84] and Guild [22]), they are frequently made and constitute a recognized general psychophysical method called by Boring [8, p. 389] "sense distance, method of fractionation." Richardson and Maxwell [59, 78, 79] and Newhall [70] have applied it to color.

VI. COMPUTED VALUES OF HUE, SATURATION, AND LIGHTNESS

Values of hue, saturation, and lightness have been computed from eq 1, 2, 3, 4, 5a, and 5c for the 15 samples used in the preliminary experiments and for 3 hypothetical nonselective samples identified by the appropriate Munsell notations, N 2/, N 5/, and N 9/.[14] These computations refer to all five illuminants studied and to observing situations described under cases 3 and 4. Values of hue and saturation have also been computed for cases 1 and 2.

TABLE 6.—*Constants used in computing the trilinear coordinates* (r_n,g_n,b_n) *of the achromatic points for the five illuminants studied (eq 3)*

Illuminant	r_f $(=r_0)$	g_f $(=g_0)$	b_f $(=b_0)$	D_f	T_{2848}	I	$\bar{A}$	A_0	A_f (eq 5a)
						fc			
Abbot-Priest sunlight	0.458	0.458	0.084	0.02		50	0.287	0.10	0.194
								.80	.544
Red	.958	.042	.000	.68	0.052	36	.330	.10	.215
								.80	.565
Yellow	.705	.295	.000	.33	.362	253	.298	.10	.199
								.80	.549
Green	.372	.613	.015	.18	.038	27	.282	.10	.191
								.80	.541
Blue	.237	.351	.412	.40	.0061	4	.272	.10	.186
								.80	.536

[14] These hypothetical samples because of their nonselectivity have trilinear coordinates (r,g,b) the same as those given in table 5 for MgO. They have been assigned values of apparent reflectance: 0.036, 0.193, and 0.738, respectively.

In table 6 are given values of the constants used in computing, by means of eq 3, the trilinear coordinates (r_n,g_n,b_n) of the achromatic points for viewing by case 3 for the five illuminants. Since the samples and background taken together are nearly nonselective in spectral reflectance, trilinear coordinates (r_f,g_f,b_f) for the field points are taken equal to those for the illuminant points (r_0,g_0,b_0) which, in turn, are taken equal to the trilinear coordinates (r,g,b) for MgO in table 5 by the assumption that MgO is spectrally nonselective [75]. The illuminances (I) supplied by the chromatic illuminants are computed as 700 T_{2848}, where T_{2848} is the transmission of the chromatic filter for light of color temperature 2,848° K. Values of T_{2848} were computed in the usual way [23, 39] from values of spectral transmission given in table 4.

Application of the constants in table 6 to eq 3 gives the following specification of the trilinear coordinates (r_n,g_n,b_n) of the achromatic point as a function of lightness, L':

Illuminant	Equation 3
Abbot-Priest sunlight	$\begin{cases} r_n=0.458-0.00022\ L'+\frac{0.00009}{(.00003)^{15}}\ (L')^2 \\ g_n=0.459-0.00035\ L' \end{cases}$
Red	$\begin{cases} r_n=0.958-0.0407\ L' \\ g_n=0.062+0.0175\ L' \end{cases}$
Yellow	$\begin{cases} r_n=0.705-0.0114\ L' \\ g_n=0.305+0.000165\ L' \end{cases}$
Green	$\begin{cases} r_n=0.372-0.00022\ L'+\frac{0.000124}{(.000044)^{15}}\ (L')^2 \\ g_n=0.618-0.0056\ L' \end{cases}$
Blue	$\begin{cases} r_n=0.237+0.0049\ \ L'+\frac{0.0063}{(.0022)^{15}}\ (L')^2 \\ g_n=0.363-0.00204\ L' \end{cases}$

[15] This constant refers to the dark background (A_0=0.10); the one given just above to the light background (A_0=0.80).

Figure 2 shows the locus (dotted line) of achromatic points plotted to a large scale on the Maxwell (UCS) triangle for the red illuminant. Only the extreme lower left-hand corner of the triangle (fig. 1) appears on this plot. Since eq 3 reduces for the red illuminant to a first-degree equation (see above), this locus is a straight line. The limits of the locus for samples viewed by momentary fixation (case 3) on a dark background (A_0=0.10) are shown by shaded circles, one for a dark (Bk) sample (A=0.03), and one for a light (W) sample (A=0.80); similar limits are indicated for a light background (A_0=0.80) by open circles. It will be noted that the achromatic point for the dark sample (A=0.03), whether viewed on the light or on the dark background, falls outside the region of the triangle representing mixtures of real stimuli. That is, according to eq 3, when an observer has been in a room filled with red light for 5 minutes or more, his visual mechanism is in such a state of chromatic adaptation that no sample exists of apparent reflectance as low as 0.03, such that it will look gray or black against a background of apparent reflectance, A_0=0.10, or greater. Figure 2 also shows the illuminant point (square) and the limits (crosses) of the locus of points representing the 15 samples

studied. Two of the vectors whose direction is correlated with hue according to eq 2 are also shown; the one associated with a dark sample viewed on a light background indicates a blue hue, the one associated with a light sample on a light ground indicates a yellow-red hue; see graphical representation of eq 2 identifying hue with direction on the triangle, shown in the upper left-hand portion of the figure.

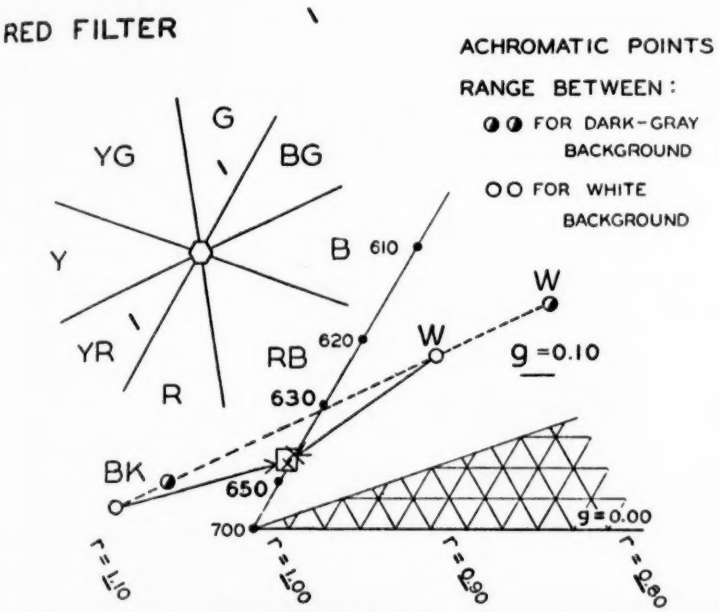

Figure 2.—*Large-scale plot of a portion of figure 1, which shows, for the red illuminant (square), the locus of the achromatic points (dotted line) and two of the vectors defining hue and saturation by eq 1, 2, and 3.*

The definition of hue, according to angle by eq 1, is indicated in the upper left-hand part of this figure. The vector indicating a blue hue refers to a dark nonselective sample on a light ground; and that indicating yellow-red hue, to a light nonselective sample on a light ground. Both vectors refer to momentary fixation of the samples by an observer who has been exposed to the field with red illumination for 5 minutes or more (case 3, section III, 2, (e)).

Figure 3 shows loci of achromatic points for all five illuminants studied. Like the locus for the red illuminant, that for the yellow illuminant is a straight line; the other loci are parabolas, those for Abbot-Priest sunlight and the green illuminant being relatively short because of the relatively small chromatic adaptation (measured by D_f) associated with them according to eq 3; note particularly the short locus for Abbot-Priest sunlight, which falls entirely within the square indicating this illuminant point. Note also how the direction of these loci is controlled by the position of the point, indicated by a double hexagon, whose trilinear coordinates (r=0.360, g=0.300) appear explicitly in eq 3. The graphical representation of eq 2 defining hue according to direction on this diagram is centered about the daylight point (0.44, 0.47, 0.09) indicated by a single hexagon.

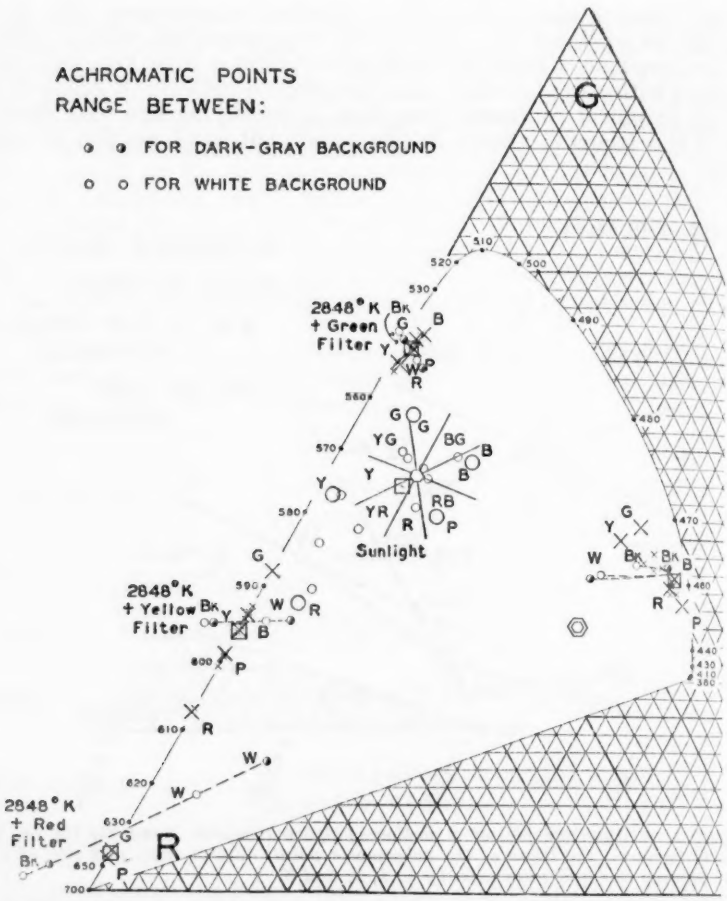

FIGURE 3.—*Loci of achromatic points (dotted lines) on the uniform-chromaticity-scale Maxwell triangle for the five illuminants studied.*

Note the varying lengths of the loci (determined chiefly by D_f), and the curvature of the loci of achromatic points for the blue illuminant (determined by b_f). Note also how the direction of each nearly straight locus is determined by the position of the point ($r=0.36$, $g=0.30$), indicated by a double hexagon, whose trilinear coordinates appear explicitly in eq 3. The definition of hue, according to angle by eq 1, is indicated graphically by lines intersecting at the daylight point (indicated by a small single hexagon).

Table 7 gives the computed hues and saturations for the hypothetical nonselective samples for both backgrounds for the five illuminants, and for the four observing situations (cases 1 to 4); it also gives lightness computed for cases 3 and 4. It should be noted that the hue to be expected for the aperture colors derived from nonselective samples (case 1) with a chromatic illuminant is approximately the hue of the illuminant, and the saturation is high. This result is independent of the apparent reflectance of the sample. Similarly, the surface color

with the illuminant color discounted (case 2) is also expected to be independent in hue and saturation of the apparent reflectance of the sample; that is, as may be seen from table 7, the colors are all expected to be achromatic (zero saturation, no hue). Cases 3 and 4 yield hues, lightnesses, and saturations for nonselective samples which depend upon the relation of the apparent reflectance, A, of the sample to that of the field, A_f. From a comparison of these computations for case 3 and case 4, the formulation may be seen to indicate that fixation of the sample for a few seconds contrary to instructions may produce a considerable change in hue and saturation of samples viewed in strongly chromatic illumination, but produces a negligible effect for samples viewed by Abbot-Priest sunlight.

TABLE 7.—*Computed hues, lightnesses, and saturations for three hypothetical nonselective samples for both light and dark backgrounds, for the five illuminants, and for four observing situations (cases 1 to 4)*

Illuminant	A_0	Sample	Computed for different viewing situations			
			Momentary fixation of sample (Case 3)	Fixation of sample for several seconds (Case 4)	Illuminant color discounted (Case 2)	Aperture color for daylight-adapted eye (Case 1)
Abbot-Priest sunlight	0.80	N 2/0	RB 0.2/0.2	RB 0.3/0.2	N /0.0	YR /1.1
		N 5/0	RB 3.5/0.1	RB 5.3/0.1	N /0.0	YR /1.1
		N 9/0	N 8.8/0.0	Y 9.4/0.1	N /0.0	YR /1.1
	.10	N 2/0	RB 0.3/0.1	RB 0.6/0.1	N /0.0	YR /1.1
		N 5/0	N 5.2/0.0	N 6.9/0.0	N /0.0	YR /1.1
		N 9/0	YG 9.4/0.1	YG 9.7/0.1	N /0.0	YR /1.1
Red	.80	N 2/0	B 0.2/6.3	B 0.3/5.2	N /0.0	YR /33.9
		N 5/0	RB 3.5/1.8	R 5.3/1.7	N /0.0	YR /33.9
		N 9/0	YR 8.7/6.8	YR 9.4/5.8	N /0.0	YR /33.9
	.10	N 2/0	B 0.3/4.3	B 0.6/2.3	N /0.0	YR /33.9
		N 5/0	YR 5.0/4.6	YR 6.9/5.1	N /0.0	YR /33.9
		N 9/0	YR 9.3/12.0	YR 9.7/7.8	N /0.0	YR /33.9
Yellow	.80	N 2/0	B 0.2/2.3	B 0.3/2.0	N /0.0	YR /16.5
		N 5/0	RB 3.5/0.9	R 5.3/0.6	N /0.0	YR /16.5
		N 9/0	Y 8.8/1.9	Y 9.4/1.6	N /0.0	YR /16.5
	.10	N 2/0	RB 0.3/1.7	RB 0.6/1.1	N /0.0	YR /16.5
		N 5/0	YR 5.1/1.3	Y 6.9/1.4	N /0.0	YR /16.5
		N 9/0	Y 9.4/3.6	Y 9.7/2.2	N /0.0	YR /16.5
Green	.80	N 2/0	RB 0.2/1.3	RB 0.3/1.1	N /0.0	G /8.8
		N 5/0	RB 3.5/0.5	RB 5.3/0.2	N /0.0	G /8.8
		N 9/0	YG 8.8/0.7	YG 9.4/0.6	N /0.0	G /8.8
	.10	N 2/0	RB 0.3/0.9	RB 0.6/0.6	N /0.0	G /8.8
		N 5/0	YG 5.2/0.4	YG 6.9/0.4	N /0.0	G /8.8
		N 9/0	YG 9.4/1.6	YG 9.7/0.9	N /0.0	G /8.8
Blue	.80	N 2/0	RB 0.2/2.5	RB 0.3/1.9	N /0.0	RB /20.0
		N 5/0	RB 3.5/0.9	RB 5.3/0.9	N /0.0	RB /20.0
		N 9/0	B 8.8/4.7	B 9.4/3.4	N /0.0	RB /20.0
	.10	N 2/0	RB 0.3/1.0	RB 0.6/0.9	N /0.0	RB /20.0
		N 5/0	B 5.2/1.7	B 6.9/1.7	N /0.0	RB /20.0
		N 9/0	B 9.4/5.5	B 9.7/2.8	N /0.0	RB /20.0

The computed color descriptions for these hypothetical nonselective samples agree, in general, both for case 3 and for case 4 with experimental results by Helson [24]. Detailed comparison has yet to be carried out, but evaluations of adaptation reflectance (see table 2) suggest that improved agreement with Helson's results would be obtained by using a definition of apparent reflectance of the field, A_f, slightly different from eq 5a, and a slightly different definition of L'.

VII. COMPARISON OF COMPUTATION WITH EXPERIMENT

Table 8 summarizes the experimental results obtained in south-daylight illumination; table 9, those obtained under the four strongly chromatic illuminants studied. These tables give the average hue, lightness, and saturation of the 15 samples estimated by the 6 observers who completed the series, namely, G. B. Reimann, G. W. Haupt, B. H. Carroll, K. S. Gibson, R. S. Hunter, and D. B. Judd. The individual variation among these observers was considerably larger than the uncertainty of estimates by the two observers who made repeat runs; this individual variation is indicated in tables 8 and 9 by the ranges of the estimates of hue, lightness, and saturation. Similar individual variation is reported by Bocksch [7, p. 366]. In parallel columns are also given the results of computations of hue, lightness, and saturation for the four observing situations (cases 1 to 4).

TABLE 8.—*Comparison of observed and computed color descriptions*

[Hue, lightness, and saturation (*H L/S*) of the 15 selective samples studied. Illuminant: Abbot-Priest sunlight taken as representative of south daylight]

Sample	Average observed values, *H L/S*	Individual observer range $\Delta H\ \Delta L/\Delta S$	Computed for different viewing situations			
			Momentary fixation of sample	Fixation of sample for several seconds	Illuminant color discounted	Aperture color for daylight-adapted eye
			(Case 3)	(Case 4)	(Case 2)	(Case 1)
LIGHT BACKGROUND (A_0=0.80)						
R 3/7	R 2.6/5.1	R 1–3/2–7	**YR** 1.6/9.6	**YR** 2.6/9.6	**YR** /9.5	**YR** /10.6
R 5/10	R 5.2/10	R 4–6/10	**YR** 4.0/10.9	**YR** 5.8/10.9	**YR** /10.9	**YR** /12.0
R 7/6	R 6.9/5.8	RB–YR 5–8/3–8	YR 6.8/4.4	YR 8.2/4.4	YR /4.4	YR /5.5
YR 4/5	YR 3.8/4.8	YR 3–5/1–7	YR 3.0/7.1	YR 4.7/7.1	YR /7.1	YR /8.3
Y 5/7	gY 4.6/4.4	Y–YG 4–5/2–6	Y 4.3/4.4	Y 6.1/4.4	Y /4.4	Y /5.4
Y 7/8	Y 6.7/9.4	Y 6–8/9–10	Y 7.1/4.9	Y 8.3/4.9	Y /5.0	Y /5.9
G 3/4	yG 2.0/2.9	YG–G 1–3/1–6	G 1.7/1.9	G 2.8/1.9	G /2.0	YG /1.3
G 5/7	G 5.3/9.8	G 4–6/9–10	G 4.9/5.0	G 6.7/5.0	G /5.0	G /4.2
G 7/7	yG 7.3/5.2	YG–G 7–8/4–8	G 7.4/2.4	G 8.5/2.4	G /2.4	YG /1.9
B 3/5	B 3.0/6.2	B 2–4/5–7	B 2.1/5.3	B 3.4/5.3	B /5.2	B /4.2
B 5/6	B 4.9/7.9	B 4–6/7–9	**BG** 4.8/4.4	**BG** 6.6/4.4	**BG** /4.4	B /3.3
B 7/4	gB 7.3/3.4	BG–B 7–8/1–8	BG 7.4/1.9	BG 8.6/1.9	BG /1.9	BG /0.8
P 3/6	RB 2.9/6.8	RB 2–4/6–8	RB 2.0/3.4	RB 3.3/3.4	RB /3.3	RB /3.3
P 5/6	RB 5.1/5.3	RB 5–6/4–8	RB 4.5/1.8	RB 6.3/1.8	RB /1.8	R /2.2
PB 7/4	B 6.8/3.6	rB–B 6–7/1–8	B 6.8/1.9	B 8.1/1.9	B /1.9	**RB** /1.0

TABLE 8.—*Comparison of observed and computed color descriptions*—Continued

[Hue, lightness, and saturation (*H L/S*) of the 15 selective samples studied. Illuminant: Abbot-Priest sunlight taken as representative of south daylight]

Sample	Average observed values, *H L/S*	Individual observer range $\Delta H\ \Delta L/\Delta S$	Computed for different viewing situations			
			Momentary fixation of sample	Fixation of sample for several seconds	Illuminant color discounted	Aperture color for daylight-adapted eye
			(Case 3)	(Case 4)	(Case 2)	(Case 1)
		DARK BACKGROUND (A_0=0.10)				
R 3/7	R 3.1/5.7	R 1–5/3–8	**YR 2.7/9.6**	**YR 4.2/9.6**	**YR /9.5**	**YR /10.6**
R 5/10	R 6.0/10	RB–R 5–7/10	**YR 5.7/11.0**	**YR 7.3/10.9**	**YR /10.9**	**YR /12.0**
R 7/6	R 7.4/6.8	RB–YR 7–9/3–9	YR 8.1/4.4	YR 8.9/4.4	YR /4.4	YR /5.5
YR 4/5	YR 4.1/5.9	YR 2–5/2–9	YR 4.7/7.1	YR 6.4/7.1	YR /7.1	YR /8.3
Y 5/7	Y 4.6/4.5	Y 2–6/2–6	Y 6.0/4.5	Y 7.5/4.4	Y /4.4	Y /5.4
Y 7/8	Y 7.4/9.9	Y 6–9/9–11	Y 8.3/4.9	Y 9.0/5.0	Y /5.0	Y /5.9
G 3/4	G 2.4/2.2	G 1–4/2–4	G 2.8/1.9	G 4.5/1.9	G /2.0	**YG /1.3**
G 5/7	G 5.7/9.0	G 4–8/8–10	G 6.6/**5.0**	G 7.9/**5.0**	G /5.0	G /4.2
G 7/7	G 7.4/4.7	YG–BG 6–9/3–8	G 8.5/2.4	G 9.2/2.4	G /2.4	YG /1.9
B 3/5	B 3.2/7.2	B 2–4/7–8	B 3.3/**5.3**	B **5.1/5.3**	B /**5.2**	B /4.2
B 5/6	B 5.4/6.8	B 4–6/5–8	**BG 6.4/4.3**	**BG 7.9/4.3**	**BG /4.4**	B /3.3
B 7/4	gB 7.6/1.8	BG–B 5–10/1–4	BG 8.5/1.9	BG 9.2/1.9	BG /1.9	BG /0.8
P 3/6	RB 3.1/5.7	RB 2–4/4–9	RB 3.2/**3.4**	RB **4.9/3.4**	RB /**3.3**	RB /**3.3**
P 5/6	RB 5.2/3.8	RB 4–6/1–7	RB 6.1/1.7	RB 7.6/1.7	RB /1.8	**R** /2.2
PB 7/4	rB 7.2/1.7	RB–B 5–8/1–3	B 8.6/1.9	B 8.9/1.8	B /1.9	RB /1.0

It may be seen from table 8 that individual saturation estimates for most of the samples viewed in south daylight are notably less certain than those for hue and lightness. For example, PB 7/4 observed on the light background was called blue by five of the six observers, and reddish blue by the sixth; hence the hue range is indicated as rB–B; the lightness estimates ranged from 6 to 7, with an average of 6.8; but the saturation estimates range all the way from 1 to 8. For each of 9 of the 15 samples viewed on the light background, all 6 observers gave the same hue name; this is indicated in table 8 by expressing the hue range for each of these 9 samples with a single hue symbol (R, YR, and so on).

Whenever the computed hue, lightness, or saturation falls within the corresponding individual-observer range, we have taken it as an indication that the formulation is substantially correct; and similarly, whenever the computed saturation is 0.5 or less, and one observer reports zero saturation we have taken the computed hue to be correct even though it does not agree with reports by the other observers. Computed hues, lightnesses, and saturations which do not agree with our experimental results are given in bold-faced type for easy identification.

1. SOUTH DAYLIGHT

It will be noted from table 8 that eq 2 is fairly successful in duplicating the hue estimates, there being only 3 samples of the 15 for which the computed result by any of the cases (1 to 4) falls outside the observed range; and indeed these 3 discrepancies are by but one division of the 8-point hue scale. Two of them (R 3/7, R 5/10) could have been eliminated by abandoning the simplifying principle of making red by eq 2 the exact opposite of green.

Computation of lightness by case 3 is in even closer agreement, no discrepancy for the light background, and only one for the dark, being shown. Case 4 (eq 5c) yields consistently higher values of lightness, and for nearly half of the samples yields values too high to be acceptable. It would appear, therefore, that our observers followed instructions to judge lightness without fixating the sample in question more than a few seconds at a time; that is, eq 5a rather than eq 5c describes the observing habits of our observers in south daylight during their judgment of lightness.

In spite of the large individual variation in the estimates of saturation, eq 3 fails for about half of the samples to yield acceptable values of saturation. This failure indicates that the UCS triangle does not yield as uniform a spacing of surface colors viewed in a field subtending visual angles large relative to the macular pigment as it does for aperture colors of small angular extent (assumption (c), section III, 1). For improved agreement, the red end of the spectrum locus must be moved closer to the daylight point (0.44, 0.47, 0.09), and the yellow part must be moved further away. Experiments on relative size of small color differences between large surfaces have already yielded the same conclusion [42, 43].

It may also be noted from table 8 that the computed hues and saturations are much alike for the observing situations (cases 1 to 4) evaluated; that is, it makes little difference according to the formulation whether an observer (a) fixates the sample momentarily, or (b) for several seconds, or (c) discounts the faint yellow-red color of south daylight compared to average daylight, or (d) is even adapted to average daylight and judges the samples merely as color areas or patches of chromatic light. A far different conclusion applies, however, to strongly chromatic illuminants, as may be seen from table 9.

2. STRONGLY CHROMATIC ILLUMINANTS

Table 9 shows that the formulation is as successful for strongly chromatic illuminants as for south daylight. As before, case 3 is seen to yield nearly perfect agreement with estimated lightnesses, while case 4 yields higher lightnesses which, for about 40 percent of the sample-illuminant-background combinations, are too high to be acceptable. Figure 4 compares the average estimates of lightness

with the lightnesses computed by eq 4 and 5a (case 3) for the 15 samples both on the light and the dark background for all 5 illuminants. It is seen that the Adams and Cobb formula renders correctly the effect on lightness of changing from light to dark background, provided the apparent reflectance of the field, A_f, be computed by eq 5a, an arithmetical mean. (The quadratic mean recommended by Adams and Cobb [2] was found not to give agreement with our experimental results; neither does eq 5c give agreement.) It would seem, therefore, that our observers in their estimates of lightness followed instructions not to fixate the sample being judged too long; and,

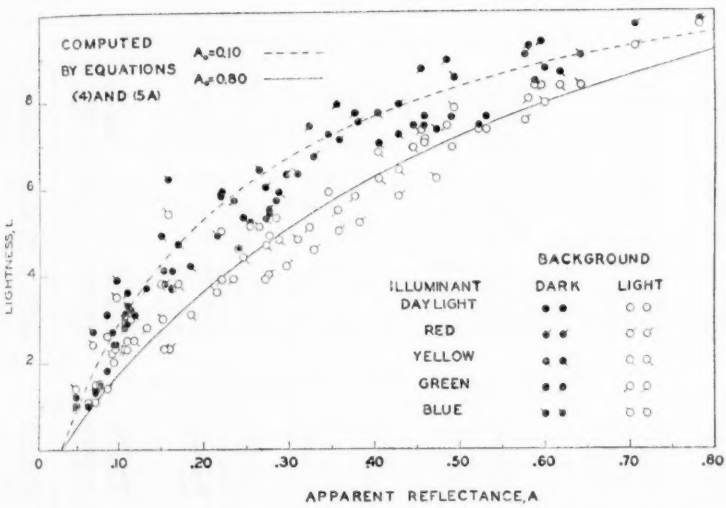

FIGURE 4.—*Comparison of estimated lightness, L, with that computed from eq 4 and 5a.*

The agreement is generally good with the exception of dark samples on a light background for nonred illuminants. See section VIII for the discussion of this discrepancy.

indeed, since light and dark samples, such as could exemplify approximately the end points (black and white) of the lightness scale, were always present in the field, there was an incentive to shift the fixation point often from the sample being judged to those representative of the end points. For estimates of hue and saturation, however, no fixed points were exemplified in the field of view, and table 9 shows that case 4 yields agreement with our observers which is not significantly different from that yielded by case 3. It is possible, therefore, that some of our observers fixated the sample whose color was being judged long enough to make case 4 apply. Case 2 gives fairly good predictions for samples on the light background, but for the red and yellow illuminants is definitely inapplicable to those on the dark. Case 1 yields hues in agreement with many of those actually reported, but, as might be expected, the saturations are much higher than those reported.

TABLE 9.—*Comparison of observed and computed color descriptions*

[Hue, lightness, and saturation (*H L/S*) of the 15 selective samples studied under the 4 chromatic illuminants; see table 4]

Sample	Average observed values, *H L/S*	Individual observer range, $\Delta H\ \Delta L/\Delta S$	Computed for different viewing situations			
			Momentary fixation of sample	Fixation of sample for several seconds	Illuminant color discounted	Aperture color for daylight-adapted eye
			(Case 3)	(Case 4)	(Case 2)	(Case 1)
RED ILLUMINANT, LIGHT BACKGROUND (A_0=0.80)						
R 3/7	bR 4.0/1.2	RB–YR 3–5/0–4	R 4.7/1.7	YR 6.6/3.0	YR /0.2	YR /34.1
R 5/10	rYR 9.2/1.4	R–rY 8–10/0–4	YR 8.5/6.6	YR 9.3/5.9	YR /0.1	YR /33.9
R 7/6	YR 9.7/1.3	yR–rY 8–10/0–4	YR 9.0/7.0	YR 9.5/6.1	N /0.0	YR /33.9
YR 4/5	bR 4.2/1.1	RB–YR 3–5/0–4	R 5.0/1.9	YR 6.8/3.1	YR /0.1	YR /33.9
Y 5/7	bR 3.9/1.0	RB–YR 3–5/0–4	R 4.6/1.5	YR 6.5/2.7	BG /0.1	YR /33.8
Y 7/8	yR 7.5/1.0	R–YR 6–9/0–2	YR 7.7/5.3	YR 8.8/5.3	N /0.0	YR /33.9
G 3/4	B 1.1/1.9	BG–BR 0–2/0–6	B 1.1/4.9	B 2.1/3.3	YR /0.2	YR /34.1
G 5/7	B 1.4/1.9	BG–RB 1–2/0–6	B 1.5/4.8	B 2.5/3.0	BG /0.4	YR /33.6
G 7/7	yR 4.6/1.1	R–YR 4–6/0–4	R 5.4/2.0	YR 7.1/3.3	BG /0.1	YR /33.7
B 3/5	gB 1.1/1.8	BG–B 0–2/0.6	B 0.9/5.3	B 1.6/3.6	N /0.0	YR /33.9
B 5/6	RB 2.3/1.4	B–R 1–4/0–6	B 2.9/2.6	RB 4.6/1.5	YR /0.1	YR /33.9
B 7/4	yR 5.2/1.0	R–YR 4–6/0–4	YR 6.0/2.7	YR 7.6/3.8	BG /0.1	YR /33.8
P 3/6	RB 2.3/1.5	B–YR 1–4/0–6	B 2.7/2.7	RB 4.4/1.4	YR /0.3	YR /34.2
P 5/6	bR 5.0/1.0	RB–YR 4–6/0–4	YR 5.8/2.8	YR 7.4/3.9	YR /0.2	YR /34.1
PB 7/4	R 5.8/1.3	RB–YR 5–7/0–4	YR 6.5/3.6	YR 7.9/4.3	YR /0.1	YR /34.0
RED ILLUMINANT, DARK BACKGROUND (A_0=0.10)						
R 3/7	YR 5.5/3.4	YR 5–6/2–5	YR 6.3/7.0	YR 7.8/6.3	YR /0.2	YR /34.1
R 5/10	YR 9.7/6.3	YR 7–11/3–12	YR 9.2/11.8	YR 9.6/7.8	YR /0.1	YR /33.9
R 7/6	YR 9.8/6.3	YR 7–11/3–12	YR 9.4/12.2	YR 9.8/7.8	N /0.0	YR /33.9
YR 4/5	YR 6.3/4.1	YR 5–7/3–6	YR 6.6/7.1	YR 8.0/6.1	YR /0.1	YR /33.9
Y 5/7	YR 6.0/3.4	YR 5–8/2–5	YR 6.2/6.5	YR 7.8/6.0	BG /0.1	YR /33.8
Y 7/8	YR 9.0/6.0	YR 7–10/3–11	YR 8.6/10.7	YR 9.3/7.5	N /0.0	YR /33.9
G 3/4	RB 1.3/0.4	RB–R 1–2/0–2	RB 1.9/1.9	R 3.5/2.0	YR /0.2	YR /34.1
G 5/7	R 1.8/0.6	RB–R 1–3/0–4	RB 2.4/1.5	YR 4.2/2.0	BG /0.4	YR /33.6
G 7/7	YR 6.7/3.9	YR 6–8/3–6	YR 6.9/7.6	YR 8.3/6.2	BG /0.1	YR /33.7
B 3/5	RB 1.0/0.6	B–RB 0–2/0–4	B 1.6/2.3	R 3.0/1.5	N /0.0	YR /33.9
B 5/6	YR 3.7/1.7	R–YG 3–4/1–4	YR 4.4/3.5	YR 6.3/4.4	YR /0.1	YR /33.9
B 7/4	YR 7.5/4.6	YR 6–8/3–8	YR 7.4/8.4	YR 8.6/6.7	BG /0.1	YR /33.8
P 3/6	rYR 3.8/2.0	R–YR 3–4/1–4	YR 4.2/3.5	YR 6.1/4.4	YR /0.3	YR /34.2
P 5/6	YR 6.9/4.2	YR 5–8/2–8	YR 7.2/8.4	YR 8.5/6.8	YR /0.2	YR /34.1
PB 7/4	YR 7.9/5.0	YR 6–9/3–10	YR 7.8/9.4	YR 8.8/7.2	YR /0.1	YR /34.0
YELLOW ILLUMINANT, LIGHT BACKGROUND (A_0=0.80)						
R 3/7	rBR 3.8/10.0	RB–R 3–6/4–16	R 2.8/6.3	R 4.4/6.5	YR /6.2	YR /22.4
R 5/10	yR 6.8/9.7	R–YR 5–9/5–16	YR 6.3/7.3	YR 7.8/7.5	YR /6.4	YR /22.7
R 7/6	rYR 8.3/6.1	R–Y 8–10/3–10	YR 8.0/4.2	YR 9.0/4.1	R /2.8	YR /19.1
YR 4/5	bR 4.4/3.3	RB–Y 3–5/1–4	R 4.3/2.6	R 6.2/2.8	YR /2.1	YR /18.5
Y 5/7	YG 4.8/0.2	Y–G 4–6/0–1	RB 4.9/0.4	YR 6.7/0.5	BG /0.3	YR /16.3
Y 7/8	gY 8.3/0.4	Y–YG 8–10/0–1	Y 7.8/1.4	Y 8.8/1.4	BG /0.1	YR /16.4
G 3/4	bRB 1.5/4.2	B–RB 1–2/0–8	B 1.3/2.6	B 2.1/1.9	BG /1.3	YR /15.2
G 5/7	gBG 3.8/6.1	G–B 3–6/3–8	BG 3.1/4.8	BG 4.8/4.4	BG /4.8	YR /12.1
G 7/7	yG 6.4/4.3	YG–G 5–7/2–8	G 6.5/1.1	G 7.9/1.1	BG /1.9	YR /14.7
B 3/5	bRB 1.5/4.7	B–RB 1–2/0–10	B 1.2/2.6	B 1.9/2.1	BG /1.4	YR /15.2
B 5/6	gB 3.1/1.4	BG–RB 2–4/0–3	B 3.3/1.7	BG 5.1/1.0	BG /1.4	YR /15.1
B 7/4	yG 6.7/2.7	YG–G 5–7/1–4	YG 6.6/0.4	YG 8.0/0.5	BG /1.0	YR /15.5
P 3/6	rRB 2.5/5.5	RB–YR 2–3/2–10	RB 2.2/1.8	R 3.5/2.1	YR /1.8	YR /18.2
P 5/6	bR 4.7/3.3	RB–Y 4–6/1–4	R 4.7/2.3	YR 6.5/2.6	YR /1.8	YR /18.2
PB 7/4	YG 6.2/0.2	Y–G 5–7/0–1	YR 6.3/0.9	YR 7.8/1.1	RB /0.1	YR /16.5

TABLE 9.—*Comparison of observed and computed color descriptions*—Continued

[Hue, lightness, and saturation (*H L/S*) of the 15 selective samples studied under the 4 chromatic illuminants; see table 4]

Sample	Average observed values, *H L/S*	Individual observer range, $\Delta H\ \Delta L/\Delta S$	Computed for different viewing situations			
			Momentary fixation of sample	Fixation of sample for several seconds	Illuminant color discounted	Aperture color for daylight-adapted eye
			(Case 3)	(Case 4)	(Case 2)	(Case 1)
YELLOW ILLUMINANT, DARK BACKGROUND (A_0=0.10)						
R 3/7	bR 4.9/8.4	RB–R 4–6/7–12	**YR** 4.2/7.0	**YR** 6.1/7.2	**YR** /6.2	**YR** /22.4
R 5/10	rYR 7.7/10.4	R–YR 6–10/8–16	YR 7.6/8.5	YR 8.7/8.0	YR /6.4	YR /22.7
R 7/6	yYR 8.6/8.9	R–Y 7–10/6–16	YR 8.9/5.6	YR 9.4/4.6	R /2.8	YR /19.1
YR 4/5	YR 5.3/5.2	YR 3–6/4–7	YR 5.9/3.6	YR 7.6/3.5	YR /2.1	YR /18.5
Y 5/7	gY 5.8/3.5	Y–YG 5–6/1–6	Y 6.5/1.8	Y 8.0/3.6	**BG** /0.3	**YR** /16.3
Y 7/8	gY 8.4/6.6	Y–yYG 7–10/2–14	Y 8.8/3.1	Y 9.4/2.0	**BG** /0.1	**YR** /16.4
G 3/4	yG 1.5/0.6	YG–G 1–2/0–2	**B** 2.2/1.4	**BG** 3.6/0.7	**BG** /1.3	**YR** /15.2
G 5/7	G 4.7/8.6	G 4–6/7–12	G 4.7/3.8	G 6.5/3.7	**BG** /4.8	**YR** /12.1
G 7/7	gYG 7.2/6.6	YG–G 6–8/4–10	YG 7.8/1.9	YG 8.8/1.4	**BG** /1.9	**YR** /14.7
B 3/5	yG 1.4/0.4	YG–G 1–2/0–2	**B** 2.0/1.4	**BG** 3.4/0.9	**BG** /1.4	**YR** /15.2
B 5/6	gYG 4.2/4.3	YG–G 3–5/3–6	YG 5.0/0.7	YG 6.8/0.7	**BG** /1.4	**YR** /15.1
B 7/4	YG 7.2/5.3	Y–G 6–8/2–8	Y 7.9/2.2	Y 8.9/1.4	**BG** /1.0	**YR** /15.5
P 3/6	rYR 3.1/3.4	R–YR 2–5/2–6	R 3.4/2.4	YR 5.2/2.6	YR /1.8	YR /18.2
P 5/6	YR 5.3/4.9	YR 4–6/3–6	YR 6.3/3.6	YR 7.8/3.3	YR /1.8	YR /18.2
PB 7/4	Y 7.0/4.7	Y–gY 6–8/2–8	Y 7.6/2.6	Y 8.7/1.9	**RB** /0.1	**YR** /16.5
GREEN ILLUMINANT, LIGHT BACKGROUND (A_0=0.80)						
R 3/7	RB 1.0/3.3	RB 1–2/0.8	**R** 0.5/2.1	**R** 1.0/1.8	**YR** /1.2	**G** /7.8
R 5/10	R 2.3/2.4	RB–yG 2–3/0–6	R 2.0/1.9	R 3.2/1.7	YR /1.3	**G** /7.7
R 7/6	rY 5.5/1.4	R–G 4–7/0–4	YR 5.8/0.5	YR 7.4/0.5	YR /0.5	G /8.4
YR 4/5	YR 2.5/2.8	R–YG 2–3/0–6	R 2.0/2.4	R 3.2/2.2	YR /1.9	YG /7.4
Y 5/7	gY 4.1/2.8	YR–YG 3–5/1–4	YR 4.0/1.5	YR 5.8/1.3	YR /1.3	YG /7.9
Y 7/8	gY 7.1/5.1	Y–YG 6–8/3–8	**YR** 6.7/1.3	**YR** 8.1/1.3	**YR** /1.3	YG /7.9
G 3/4	B 2.3/1.8	G–RB 2–3/0–6	RB 2.0/0.7	RB 3.2/0.4	G /0.4	G /9.1
G 5/7	G 5.8/2.4	G 4–8/0–4	G 6.0/0.8	G 7.6/0.9	G /0.7	G /9.4
G 7/7	G 8.3/0.9	G 7–9/0–2	G 7.9/0.8	G 8.9/0.9	G /0.4	G /9.1
B 3/5	B 2.8/3.8	B 2–4/2–6	B 2.4/1.3	**BG** 3.9/1.3	**BG** /1.3	G /9.8
B 5/6	B 5.1/3.9	B 3–6/1–7	**BG** 5.4/1.1	**BG** 7.1/1.2	**BG** /1.2	G /9.6
B 7/4	B 8.0/0.5	BG–B 6–9/0–2	G 7.8/0.8	G 8.8/0.9	BG /0.5	G /9.1
P 3/6	bRB 2.3/2.1	B–RB 2–3/0–6	RB 1.7/1.1	RB 2.8/0.8	B–RB /0.2	G /8.7
P 5/6	B 4.1/0.8	BG–RB 2–5/0–4	RB 4.2/0.4	B 6.1/0.1	BG /0.1	G /8.8
PB 7/4	B 7.2/1.0	B 6–8/0–2	G 7.0/0.7	G 8.3/0.7	**BG** /0.5	G /9.1
GREEN ILLUMINANT, DARK BACKGROUND (A_0=0.10)						
R 3/7	bR 1.0/2.2	RB–R 0–2/0–6	R 1.0/1.7	R 1.9/1.4	**YR** /1.2	**G** /7.8
R 5/10	yYR 2.9/2.4	YR–Y 2–6/1–4	YR 3.2/1.4	YR 4.9/1.3	YR /1.3	**G** /7.7
R 7/6	gY 7.7/3.6	Y–YG 6–10/1–10	YG 7.2/0.9	Y 8.4/0.8	**YR** /0.5	**G** /8.4
YR 4/5	yYR 3.6/3.8	YR–Y 3–6/2–6	YR 3.2/2.0	YR 4.9/1.9	YR /1.9	**YG** /7.4
Y 5/7	gY 6.1/4.8	Y–YG 4–8/2–10	Y 5.6/1.4	Y 7.3/1.3	**YR** /1.3	YG /7.9
Y 7/8	Y 8.5/6.7	Y 8–12/3–16	Y 8.0/1.6	Y 8.9/1.4	**YR** /1.3	**YG** /7.9
G 3/4	G 2.8/1.2	G 2–4/0–4	BG 3.2/0.3	G 4.8/0.4	G /0.4	G /9.1
G 5/7	yG 7.7/4.4	YG–G 7–10/2–10	G 7.4/1.6	G 8.6/1.3	G /0.7	G /9.4
G 7/7	gYG 9.3/4.6	YG–G 9–12/1–12	YG 8.8/1.7	YG 9.4/1.2	G /0.4	G /9.1
B 3/5	gB 3.7/3.2	BG–B 3–4/2–6	BG 3.8/1.3	BG 5.6/1.4	BG /1.3	G /9.8
B 5/6	gB 7.2/4.0	G–B 6–10/2–10	G 7.0/1.7	G 8.2/1.5	BG /1.2	G /9.6
B 7/4	yG 9.2/4.2	YG–G 8–12/1–12	YG 8.7/1.6	YG 9.4/1.2	**BG** /0.5	G /9.1
P 3/6	RB 2.4/0.5	RB 1–4/0–4	RB 2.8/0.4	B–RB 4.6/0.2	B–RB /0.2	**G** /8.7
P 5/6	bG 5.9/2.0	G–BG 4–8/0–6	**YG** 5.7/0.6	**YG** 7.5/0.6	BG /0.1	G /8.8
PB 7/4	G 8.7/6.1	YG–BG 8–12/2–12	YG 8.2/1.5	G 9.0/1.0	BG /0.5	G /9.1

TABLE 9.—*Comparison of observed and computed color descriptions*—Continued

[Hue, lightness, and saturation (*H L/S*) of the 15 selective samples studied under the 4 chromatic illuminants; see table 4]

Sample	Average observed values, *H L/S*	Individual observer range, ΔH $\Delta L/\Delta S$	Computed for different viewing situations			
			Momentary fixation of sample	Fixation of sample for several seconds	Illuminant color discounted	Aperture color for daylight-adapted eye
			(Case 3)	(Case 4)	(Case 2)	(Case 1)
BLUE ILLUMINANT, LIGHT BACKGROUND (A_0=0.80)						
R 3/7	rRB 1.4/1.8	RB–R 1–2/0–6	RB 0.5/2.7	RB 1.0/2.1	R /0.8	RB /20.3
R 5/10	bR 3.0/3.6	RB–R 3/2–6	RB **2.0/1.6**	RB **3.3/1.3**	R **/0.4**	RB /20.1
R 7/6	RB 5.9/3.1	RB–rRB 5–7/1–5	RB 5.7/1.3	RB 7.3/1.8	**R /0.3**	RB /20.0
YR 4/5	R 2.4/2.5	RB–YR 2–3/1–4	RB **1.1/0.2**	**Y** 1.8/0.6	**YG** /1.5	RB /18.5
Y 5/7	rYR 3.5/2.8	RB–Y 3–4/1–4	**YG 1.7/1.0**	**YG 2.9/1.6**	**YG** /2.4	RB /17.6
Y 7/8	yYR 5.4/4.6	R–Y 4–6/1–6	**YG 2.9/3.8**	**YG 4.6/3.9**	**YG** /4.6	**B** /15.6
G 3/4	bRB 2.2/0.5	B–RB 2–3/0–2	B 1.6/0.5	YG 2.8/0.3	**YG** /1.2	B /19.0
G 5/7	yG 5.1/3.8	YG–BG 4–6/2–5	YG 4.7/3.5	YG 6.5/3.4	YG /4.4	**B** /16.7
G 7/7	yG 7.6/1.5	Y–G 6–9/0–4	**BG** 7.1/1.9	**BG** 8.4/2.1	YG /2.3	**B** /18.2
B 3/5	B 3.8/2.2	B 3–4/0–4	**RB** 3.9/0.9	**RB 5.7/1.2**	B /0.3	**RB** /20.2
B 5/6	gB 6.2/4.4	BG–B 5–7/2–6	B 6.9/2.1	B **8.2/2.3**	**G /0.7**	**RB** /19.6
B 7/4	B 8.3/2.2	G–B 7–9/1–4	B 8.2/3.5	B 9.1/3.1	**YG /0.3**	**RB** /19.7
P 3/6	rB 3.0/3.4	B–RB 2–4/0–4	RB 2.8/2.8	RB 4.4/2.6	RB /1.8	RB /21.4
P 5/6	rB 4.8/2.8	R–rRB 4–5/0–5	RB 5.3/2.0	RB 6.9/2.5	RB /1.0	RB /20.8
PB 7/4	B 7.9/2.3	B 6–9/1–4	B 7.9/3.5	B 8.9/3.1	**RB /0.1**	**RB** /20.1
BLUE ILLUMINANT, DARK BACKGROUND (A_0=0.10)						
R 3/7	bR 1.2/2.0	RB–R 0–2/0–4	RB 1.0/1.7	RB 1.8/1.6	R /0.8	RB /20.2
R 5/10	rRB 3.3/4.2	RB–R 2–4/1–6	RB 3.2/1.3	RB **4.9**/1.4	R **/0.4**	RB /20.1
R 7/6	rRB 7.2/2.5	RB–R 6–8/0–4	**B** 7.2/3.1	**B** 8.4/2.3	R /0.3	RB /20.0
YR 4/5	YR 2.7/3.3	rYR–YR 2–4/2–5	**Y 2.0/1.0**	**Y** 3.3/0.8	**YG** /1.5	**RB** /18.5
Y 5/7	yYR 3.9/4.2	YR–Y 3–5/3–5	**YG 2.9/1.7**	**YG 4.6/1.5**	**YG** /2.4	**RB** /17.6
Y 7/8	rY 6.2/6.2	YR–Y 5–7/4–8	**YG 4.5/3.4**	**YG 6.2/3.3**	**YG** /4.6	**B** /15.6
G 3/4	yG 2.7/1.7	YG–G 2–4/1–3	**YG 2.8/0.4**	G 4.4/0.5	YG /1.2	**B** /19.0
G 5/7	yG 6.4/5.1	YG–G 6–7/4–8	G **6.3/3.4**	G **7.8/3.4**	YG /4.4	**B** /16.7
G 7/7	gBG 8.3/2.1	G–B 8–9/1–8	BG 8.3/3.7	BG 9.1/2.2	**YG** /2.3	B /18.2
B 3/5	B 5.1/5.1	gB–B 4–6/4–8	B **5.6/2.2**	B **7.2/2.0**	B **/0.3**	**RB** /20.2
B 5/6	B 7.3/5.5	B 7–8/4–10	B 8.2/4.1	B **9.0/2.4**	**G /0.7**	**RB** /19.6
B 7/4	B 9.0/3.4	B 8–10/1–10	B 9.0/5.1	B 9.5/2.6	**YG /0.3**	**RB** /19.7
P 3/6	bRB 4.1/4.2	B–RB 3–5/2–8	RB 4.3/2.9	RB **6.1**/3.1	RB /1.8	RB /21.4
P 5/6	rB 6.3/4.4	B–RB 6–7/3–8	B 6.8/3.7	RB **8.1/2.9**	RB **/1.0**	RB /20.8
PB 7/4	B 8.7/3.9	B 8–10/2–10	B 8.9/5.2	B 9.4/2.8	**RB /0.1**	**RB** /20.1

Table 10 summarizes the success of the formulation for the four observing situations. Each computed result, correct in the sense that it is within the range of the individual estimates, is given in tables 8 and 9 in plain (not bold-faced) type. The total numbers correct in this sense out of the 15 samples are given in table 10 for each illuminant-background combination. If the total should be listed 15 15/15, perfect agreement between formulation and preliminary experiment would be indicated for hue, lightness, and saturation; but if the total should be 0 0/0, no correspondence at all would be indicated. Totals for all illuminants are given for each

background, and grand totals for each observing situation. The grand totals are also expressed in percentages of the total number (150) of sample-illuminant-background combinations. It will be seen that the formulation for case 3 yields 97 percent of these combinations in agreement with the experiment in regard to lightness, 84 percent in regard to hue, and 73 percent in regard to saturation. The superiority of case 3 over cases 2 and 4 is gratifying, because it indicates that the attempt to take into account the actual observing situation has been largely successful. On the other hand, there is need for further work before it can be said that this success is complete.

TABLE 10.—*Number of sample-illuminant-background combinations correct*

Illuminant	Apparent reflectance of background A_0	Number correct			
		Case 3	Case 4	Case 2	Case 1
South daylight	0.80	12 15/7	12 10/7	12 /7	11 /5
	.10	12 14/7	12 8/7	12 /7	11 /6
Red	.80	15 15/12	15 7/12	15 /15	11 /0
	.10	15 15/11	14 7/13	9 /3	12 /0
Yellow	.80	14 15/13	14 9/14	10 /15	5 /0
	.10	12 15/12	12 6/10	5 /3	5 /0
Green	.80	10 15/13	9 12/13	10 /13	7 /2
	.10	14 15/12	14 12/10	10 /8	8 /8
Blue	.80	11 11/14	10 12/14	7 /10	8 /0
	.10	11 15/9	11 9/9	8 /8	6 /0
Total	.80	62 71/59	60 50/60	54 /60	42 /7
	.10	64 74/51	63 42/49	44 /29	42 /14
Grand total correct		126 145/110	123 92/109	98 /89	84 /21
Percentage correct		84 97/73	82 61/73	65 /59	56 /14

Out of the 56 combinations for which case 3 failed to yield acceptable color descriptions, all but 4 combinations can apparently be adjusted by a more careful choice of constants in the definition of L' and in eq 3, by a redefinition of hue (eq 2) without the simplifying restriction that red shall be taken as the exact opposite of green, and by the use of a coordinate system giving improved chromaticity spacing. The preliminary data do not afford a very reliable basis for such revaluation of the constants; and it is planned next to examine carefully the more complete data of Helson and Jeffers [26], which have already served as guides in several aspects of the formulation. The four combinations which are still a puzzle are two on the light background (B 7/4, PB 7/4) under the green illuminant, and two under the blue illuminant, both involving Y 7/8, one for the light, the other for the dark background. It is interesting to note that the observers reported more nearly the daylight colors of these samples than apparently can be justified from the computations, but we do not believe that the observers remembered the daylight colors. Helson and Jeffers [25, 26] find color descriptions in accord with our computations for samples B 7/4 and PB 7/4 under the green illuminant; this finding suggests an unknown source of error in our preliminary experiments.

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But they find the same colors as our observers did for sample Y 7/8 under the blue illuminant. This finding suggests that the formulation may have to be revised.

The large individual variations in estimates of saturation and the smaller variations in hue can be explained; first, by the ambiguity of the observing situation which permits allocation by the observer of any chromatic component of the illumination hue in indeterminate proportion between the illumination and the surface color;[16] and second by variations in eye movements such as distinguish case 3 from case 4. The need for these explanations in regard to saturation would be more acute, however, if our observers had agreed better in their saturation estimates in south daylight (table 8). A large part of the individual variation is to be ascribed to uncertainty inherent in our experimental method.

3. SUBSTITUTION OF A DARK FOR A LIGHT BACKGROUND

The comparison between computed and experimentally obtained hues and saturations has so far dealt only with the ranges in the experimental values. One might readily suppose that the agreement between computation and experiment for both light and dark backgrounds arises from an experimental uncertainty sufficiently large to cover any differences between them. The success of the formulation is more detailed and complete, however, than has yet been demonstrated, and to show this success we have compared the direction of hue differences computed for each sample-illuminant combination with that observed, taking the average observed values in tables 8 and 9. Similar comparisons have been made for the direction of lightness and saturation differences and have been summarized in table 11. It will be noted that for about 65 percent of the sample-illuminant combinations the computed change agrees with that indicated by the average of the actual estimates in the sense that for these combinations either the direction of the difference agrees, when both observed and computed differences are significant, or both computed and observed differences are too small to be significant. About 33 percent of the combinations show disagreement in the limited sense either that no significant difference was observed even though predicted by the computation, or the reverse. There are 28 combinations (37 percent) which showed limited disagreement of this sort in lightness; for these combinations no significant difference was observed from substitution of a dark for a light background, but eq 4 indicates for each combination an increase in lightness greater than 0.5. This may also be seen from figure 4. It is probably significant that nearly all (13 out of 15) of the samples viewed by south daylight fall in this category. Helson [25–26] has discussed the conditions under which the expected increase in lightness is found by observation.

[16] Katz [48, p. 219] ascribes the large individual differences principally to differences in attitude. Gelb [16, p. 677] likewise mentions attitude, which he found to be "fluctuating and unstable," corresponding to different organizations of the visual field. This view is close to ours in section III, 2, (c).

TABLE 11.—*Effect on the color of a sample caused by substitution of a dark for a light background*

HUE

Computed ↓ / Observed →	Number of sample-illuminant combinations: Observed to change in the RYGBR sense by more than one-sixteenth of the hue circuit	Observed to change by less than one-sixteenth of the hue circuit	Observed to change in the RBGYR sense by more than one-sixteenth of the hue circuit
Computed to change in the RBGYR sense	0	5	7
Same hue on the 8-point hue scale	6	32	3
Computed to change in the RYGBR sense	13	8	1

LIGHTNESS

Computed ↓ / Observed →	Number of sample-illuminant combinations: Observed to decrease by more than 0.5	Observed to change by 0.5 or less	Observed to increase by more than 0.5
Computed to increase by more than 0.5	0	28	44
Computed to change by 0.5 or less	0	3	0
Computed to decrease by more than 0.5	0	0	0

SATURATION

Computed ↓ / Observed →	Number of sample-illuminant combinations: Observed to decrease by more than 0.5	Observed to change by 0.5 or less	Observed to increase by more than 0.5
Computed to increase by more than 0.5	3	1	34
Computed to change by 0.5 or less	8	5	14
Computed to decrease by more than 0.5	8	1	1

The combinations showing direct contradiction between computation and experiment are few; one in hue, none in lightness, and four in saturation. The contradiction in hue is found for sample PB 7/4 under the yellow illuminant (see table 9); the computed hue change is from YR to Y; the observed, from YG to Y. There is some doubt as to the significance of this apparent contradiction because of the low saturation (0 to 1) of the reported color. The four contradictions in saturation are found for samples R 3/7, G 5/7 and P 3/6 under the yellow illuminant, and R 7/6 under the blue (see table 9). These discrepancies are by about 2 steps on the saturation scale of 10; considering the large individual variation in estimates of saturation, a few such contradictions are to be expected even in an average of estimates

by six observers. At least one observer corroborated each computed result. It may be concluded that the formulation is successful in specifying the observed effect on color of the sample caused by substitution of a dark for a light background.

VIII. INFLUENCE OF LIGHT-SCATTERING ELEMENTS BETWEEN SAMPLE AND RETINA

If the optical media between the sample plane and the retinal image of that plane contain light-scattering elements, it is to be expected that the aperture colors corresponding to all surfaces will be modified in the sense corresponding to admixture of light reflected from the field as a whole. The amount of the admixture would correspond to the number of light-scattering elements; these elements might be in the space between the observer and the samples (air molecules, dust, or fog), on the surface of the filters through which the observers looked (imperfect polishing of the surface, dust, or grease), or in the optical media of the eye itself (incipient cataract, floating particles in the aqueous humour, inclusions, or haze in the vitreous humor). Although such elements were present in all these places, no specific account of them has been taken; first, because it has been assumed that the amount of light scattered by them is too small to produce a significant effect; and second, because such light would chiefly serve as a clue to the illumination [10] rather than influence the estimates of hue, lightness, and saturation of the surface color.

Certain aspects of the formulation and comparison with experiment indicate, however, that the influence of light-scattering elements may not be negligible. The situation in which such influence would make itself most evident is the observation of dark samples on a light background. Light from the background would be scattered onto the retinal image of the dark sample, and even though amounting to a very small fraction of the retinal illuminance corresponding to the background, it might constitute a considerable fraction of that corresponding to the dark sample itself. In such a case the chromaticity of the color would be altered toward that of the scattered light, and the observed lightness would be higher than could be accounted for by eq 4. Reference to figure 4 shows, except for the red illuminant, that all samples of apparent reflectance less than 0.18 were observed to have lightnesses higher than those computed from eq 4, the discrepancies being particularly large for the blue illuminant. It may therefore be significant that in table 9 the only sample-illuminant-background combinations yielding computed values too low to fall within the individual variation are four samples of low apparent reflectance on the light background under the blue illuminant. These discrepancies suggest the presence of light-scattering elements in the eye media so small that they are selective in their scattering power, scattering more short-wave than long-wave light somewhat in accord with the Rayleigh law that such scattering is inversely proportional to the fourth power of the wavelength. Light-scattering elements of this sort were postulated by Holladay [32] to explain certain of his measurements on the amount of stray light in the eye. Further studies of this quantity have been carried out by Bartley and Fry [5], by le Grand [20] and by Schouten [81]. Helmholtz [30, p. 274, 278]

suggested that fluorescence of the eye media, as well as scattering of light, might be a contributing cause.

It should be noted in this connection that a part of the effect of the $(L')^2$ term in the formula for r_n (eq 3) is to contribute to a red-blue component for dark samples on a light ground. This component is proportional to the apparent reflectance, A_f, and blue trilinear coordinate, b_f, of the field; so it is already closely of the form required to take account of Rayleigh scattering by the eye media. Since this term combined with 0.030 D_f in the expression for g_n agrees qualitatively with Karwoski's findings [46] of the prevalence of red-blue in the after-images produced by intense stimuli, we have so far viewed it as an approximate representation of some photochemical or neurological fact of the retina or central nervous system. Perhaps, however, it is to be considered as partly based upon Rayleigh scattering and fluorescence by the eye media. A better approximation to Rayleigh scattering could be obtained by the substitution of the term $1+10b_f$ for b_f; and it might also be worth while to modify eq 4 by the appropriate introduction of such a term. Appraisal of the value of such modifications will be easier after a detailed check of the formulation against the extensive experimental results of Helson and Jeffers [26] has been carried out.

IX. BEZOLD-BRÜCKE PHENOMENON AND THE HUE CHANGE BY ADMIXTURE OF ACHROMATIC LIGHT

It was observed by Von Bezold [6] and by Brücke [9] that an increase in luminance not only increases the brightness of the aperture color but also introduces a change in hue. Red, yellow-red, and yellow-green shift toward yellow; red-blue and blue-green toward blue. By reverse application of assumption (d) (section III) it will be noted that the present formulation should apply to this hue change, often called the "Bezold-Brücke" phenomenon. Inspection of eq 3 shows that the formulation agrees in a broad way with the Bezold-Brücke phenomenon, provided the formulation be rewritten to apply to aperture colors by substitution of luminance for apparent luminous reflectance, A. There have been some quantitative studies of this phenomenon, notably by Janicki and Lau [36] and by Purdy [76],[17] against which it is possible to check the present formulation, and, perhaps, obtain better values for the constants; but computations by eq 1 and 3 for comparison with these quantitative results have not yet been made.

The hue change by admixture of achromatic light has been studied by Müller [77] both for dark and for light backgrounds, and by Abney [1] for dark background. Abney found red, yellow-red, and yellow-green to shift toward yellow, and red-blue to shift toward red. The hue change for a light background is analogous to that for dark with colors of red-blue hue, but reverses for red, yellow-red and yellow-green, which shift away from yellow. It may be shown from eq 3 that the present formulation is in qualitative agreement with these known facts, but quantitative comparison has yet to be made.

These hue changes by change of luminance and by admixture of achromatic light make the concept of dominant wavelength an unre-

[17] Consult Purdy [76] for 14 other references to the Bezold-Brücke phenomenon, experimental and theoretical.

liable indication of hue. The present formulation may therefore lead to a substitute for dominant wavelength by means of which colorimetric results (such as obtained by the spectrophotometer) may be interpreted in accord with the actual hue of the surface color. Aids to computation of hue by eq 1, which would make it readily applicable in practice, have yet to be worked out.

X. RELATION TO VISUAL THEORY

The present formulation giving approximately the hue, saturation, and lightness of a surface color in any of a wide variety of illuminants for both light and dark backgrounds is, of course, in no sense a theory of vision. It does not separate photochemical activity from neural activity in the retina, nor retinal activity from cortical, nor even photochemical effects from fluorescence and scattering of light by the optical media of the eye. The primaries of the coordinate system used are not intended to represent colors produced by structurally or functionally separated parts of the visual mechanism; they merely compose one of an infinite number of sets giving approximately uniform chromaticity spacing. It is true that the $(L')^2$ term is confined in eq 3 to the expression for r_n; similarly the term $0.030D_f$ in the expression for g_n finds no counterpart in the expression for r_n. This simplicity does not however, indicate a fundamental significance to be attached to the primaries of the coordinate system so much as it indicates the preliminary character of eq 3, which has been derived empirically. Probably, further work will show the necessity of a small $(L')^2$ term in the equation for g_n, and of a term composed of D_f multiplied by a small constant in that for r_n. The sole reason for choice of the coordinate system used is its degree of approach to uniform chromaticity spacing, and it would be logical to transfer the formulation to some other coordinate system if one could be devised to yield a more uniform chromaticity-spacing.

The validation of the present empirical formulation does, however, clear the ground for the construction of a theory. The relation of the chromatic components (hue and saturation) of the surface color to the corresponding aperture color and the different character of the correspondence between the achromatic components (lightness and brightness) foreshadowed by the work of Bocksch [7, p. 395] has been formulated and verified. The variables defining the viewing situation (A_f, r_f, g_f, b_f) have been formulated and their effect upon hue, saturation, and lightness of the surface color have been quantitatively evaluated within a coordinate system defined in terms of the standard ICI system [23, 39]. Various components of these effects have been well known, but the total amounts of them have not been evaluated until now.

From the variables found to be pertinent in defining the viewing situation it may be concluded that the more familiar theories of vision (Helmholtz, Hering, Ladd-Franklin) require elaboration before they are applicable to this problem. These theories refer with some adequacy to aperture color with a dark surrounding field but not to the more complicated situation of objects in an illuminated space. The suggestion by Ives [34] for an extension of the Helmholtz theory [30, p. 235, 276] to this case is seen (section III, 2, (e)) to be an approximation to the truth for the limited groups of samples for which

$A \doteq A_f$, for illuminants that are not too selective, and probably also for durations less than 10 seconds. It may be seen from figures 2 and 3, however, that some strongly selective illuminants give rise to achromatic points which are outside the region corresponding to real stimuli. We may conclude, therefore, that to follow out Ives' suggestion would require a coordinate system in which the spectrum locus falls well inside the Maxwell triangle, such as those suggested by Helmholtz [28] and Sinden [83] on other grounds.

The theory of G. E. Müller [64] goes far toward allocation of the various color effects to activities of one or another portion of the visual mechanism, and it is furthermore elaborated to take account of light and dark surrounding fields. The information supplied by our formulation might be used to quantify the Müller theory. An initial difficulty arising from lack of any distinction in the Müller theory between brightness and lightness has been discussed by Bocksch [7, p. 436ff], who suggested a way of elaborating the Müller theory in this respect. To extend the Müller theory, however, to the perception of object and illumination color (Katz [48], Gelb [16]) in such a way as to embrace the present formulation, including the appearance of surface-color hues nearly complementary to the illuminant hue by after-image projection would be a long, involved task; but an attempt might be worth while because any resultant quantitative color theory would stimulate further visual research by being amenable to quantitative verification.

XI. SUMMARY

The stimulus for an aperture color can be expressed as a function of three variables. Surface color, however, includes the idea of a surface viewed in the presence of other surfaces in an illuminated space; it requires at least six variables. The observer may perceive the visual field yielded by such surfaces as a pattern of juxtaposed color areas, or aperture colors; or he may perceive this field organized into objects in an illuminated space. The surfaces of the objects possess surface colors, and the space possesses an illumination color; surface color and illumination color are both related to the pattern of aperture colors, illumination color being derived from clues obtained from the whole visual field and its organization. Simple visual fields, such as those studied here, can be produced by more than one combination of objects with illumination, and accordingly, it is usual to find that observers will report more than one organization of them. This ambiguity generates large individual variations. Other variations arise because the eye movements of the observer are uncontrolled; that is, the surface color may depend somewhat upon whether he has just previously been looking at the darkest or the lightest object in the field.

From a study of the literature, formulas for hue, lightness, and saturation of surface colors have been set up for all illuminants (daylight and chromatic); for all backgrounds (black, gray, white, and chromatic); and for four viewing situations. These formulas for the most common viewing situation are based upon the principle known in Helmholtz' time [30, p. 267] that the hue and saturation of the surface color seen at any given instant are the result of projecting upon the field provided by the surface an after-image of the average field

seen for the previous 15 or 20 seconds. It has been found impractical to represent changes in retinal sensitivity which produce these afterimages by changes in coordinate system so as to make achromatic colors correspond to equal stimulation of the red, green, and blue processes, as in the Young-Helmholtz theory. Instead, the same coordinate system has been used for all states of chromatic adaptation, a central part of the formulation being the definition of the trilinear coordinates of the point in this system representing for each state of adaptation the stimulus for an achromatic color. This achromatic point is found to wander about in the neighborhood of the point representing the average of the visual field. There is, therefore, scarcely any real stimulus which cannot under some viewing situation give rise to an achromatic color, and, indeed, many of the achromatic points are to be found outside of the area representing real stimuli (that is, outside of the area of the Maxwell triangle bounded by the spectrum locus and the straight line joining its extremes).

The formulas have been checked and their constants approximately evaluated by means of preliminary observations by 6 observers viewing 15 samples of known spectral apparent reflectance under 5 illuminants (daylight and four strongly chromatic illuminants) of known spectral-energy distribution with two spectrally nonselective backgrounds (in daylight, dark gray, and white) of known apparent reflectance. The formulas have been improved by a preliminary study of more careful and extensive observations of the same samples under the same illuminants by Helson [24, 25, 26]. The hues, lightnesses, and saturations computed by the improved formulas have been compared with the present results and have been shown to be in agreement with estimated lightness in 97 percent of the 150 sample-illuminant-background combinations studied, to be in agreement with estimated hue in 84 percent, and to be in agreement with estimated saturation in 73 percent of the combinations studied. The connection of the formulas to theories of vision has been pointed out, and there has been given a brief discussion of their application to visual phenomena known by various names (the "dimming effect," light-scattering by the optical media of the eye, Bezold-Brücke phenomenon, and the hue change by admixture of achromatic light).

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COMBINATION OF WOOL PROTEIN WITH ACID AND BASE: HYDROCHLORIC ACID AND POTASSIUM HYDROXIDE [1]

By Jacinto Steinhardt and Milton Harris [2]

ABSTRACT

As an initial part of a general program for the study of the acidic and basic characteristics of textile fibers, a study has been made of the dependence on pH of the amounts of hydrochloric acid and of potassium hydroxide taken up by wool from aqueous solutions. The effect on this dependence of the maintenance of a constant ionic strength by additions of a neutral salt, potassium chloride, has also been determined. Most of the measurements were made at 0° C to minimize the effects of decomposition brought about by exposure to extreme concentrations of acid or base.

The maximum acid-binding capacity, independent of ionic strength, is 0.82 millimole per gram; the maximum base-binding capacity is greater than 0.78 millimole. With salt absent, no appreciable binding of acid or base occurs in the pH interval, 5 to 10, but the amount bound increases very sharply as these limits are exceeded. When salt is present, the amount of acid or base bound changes with pH more gradually, and there is no wide region in which combination fails to occur; the point of zero combination is sharply defined and is near pH 6.4. The positions of the titration curves with respect to the pH axis are different at every ionic strength. The differences are larger than can be attributed to the effect of salts on the dissociation of acids; thus, in dilute solutions an n-fold change in the total concentration of chloride ions produces a change almost as great as would be produced by a similar n-fold change in the concentration of hydrogen ions. This approach to stoichiometric dependence of the acid bound on the concentration of anions as well as of hydrogen ions accounts for the greater steepness of the titration curve when the source of both ions is the acid alone.

The dependence of acid bound on anion concentration or base bound on concentration of cations is explained by treating the electrostatic restrictions arising from the existence of two phases as a case of partial dissociation of protein salts. A possible alternative analysis by means of the Donnan equilibrium is also presented, and factors to be considered in making a final choice between the two treatments are described in detail. Either analysis predicts that the positions of the curves with respect to the pH axis should, at high salt concentrations, approach a limit which should correspond to the titration curve of the same protein in the dissolved state. This prediction is supported by the fact that the data for wool agree very closely at high salt concentrations with those for a similar but soluble protein, egg albumin.

On the basis of this comparison, a detailed analysis is undertaken of the composition of the titration curve in terms of the constituent di-acidic and di-basic amino acids of wool. This analysis leads to the conclusion that the binding of acid and base by wool occurs at the free carboxyl, imidazole, amino, and guanidino groups, but that no combination of base with the tyrosine hydroxyl group takes place in the pH range of this investigation.

[1] The state of combination of wool with acid and base is intimately related to its ability to absorb moisture and dyes, its elastic and tensile properties, and its behavior in carbonizing, scouring, and milling. In order to form a background for researches relating to these technologically significant properties of wool, an extensive investigation on the acidic and basic properties of the fibers has been undertaken.

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I. INTRODUCTION

The nature of the dependence on pH of the degree of combination of acid and base by such insoluble proteins as wool, silk, and collagen differs in certain characteristic ways from that of soluble proteins. The examination of measurements reported by Speakman and Hirst [43],[3] Lloyd and Bidder [34], and others leads to the conclusion that the titration curves of these three proteins, determined in the absence of salt, are distinguished from those of all soluble proteins so far studied [4] under the same conditions in three principal respects:

1. They show a long region of little or no acid- or base-binding capacity, more or less symmetrically placed about the point of neutrality. This is true even when, as in the case of wool and silk, they contain appreciable quantities of histidine which, because of its imidazole group, should function as a buffer in this region.

2. The amounts of acid and base bound increase sharply as the extremes of the pH scale are approached and reach their respective maximum values at about the same pH as in the case of soluble proteins. Thus, the titration curves are steeper than those of soluble proteins, or of soluble polybasic acids in general.

3. The pH values at which half of the maximum amount of acid or base is combined (a convenient measure of the position of the curve and, in simple substances, directly related to the acid strengths of the groups titrated), are shifted considerably toward the two extremes of the pH scale. Thus, the S-shaped portions of the curves found on the acid side of pH 7 are centered, in the case of almost all dissolved proteins, about a pH very close to 4.0, but in earlier published work on wool this point appears to be 2.3 [43, 44, 45]. If these curves are regarded as resulting from the titration of many groups which possess identical dissociation constants this difference in the position of the midpoints would represent a fifty-fold increase in the acid strength of the insoluble protein, although its dissociating groups are presumed to be the same as those present in proteins which may be titrated in the dissolved state.

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[3] Figures in brackets indicate the literature references at the end of this paper.
[4] Except those, such as hemoglobin, in which irreversible effects occur [10, 37].

This description of the striking differences between the titration curves of soluble and insoluble proteins is made more concrete by the comparison in figure 1 of the data for wool (obtained as described in the experimental section) with similar data of Kekwick and Cannan [31] for the soluble protein, egg albumin, both at 25° C. The latter are chosen because of their general excellence, and the close similarity in relative composition of egg albumin and wool, with respect to those amino acids (aspartic acid, glutamic acid, and histidine) which should affect the shape and position of their titration curves [5] in the acid region, although these proteins differ con-

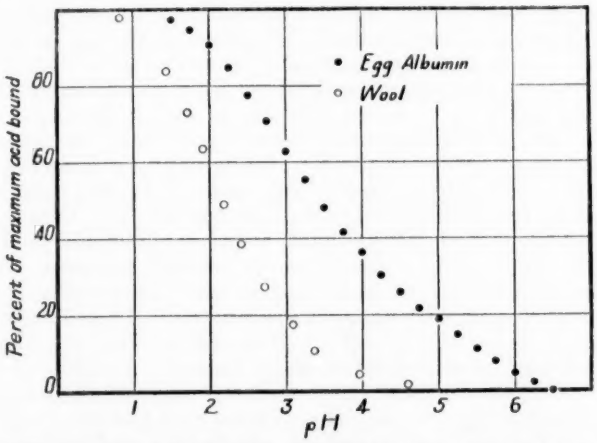

FIGURE 1.—*Comparison of the curves of acid combination of wool and of egg albumin at 25° C, in the absence of added salt.*

siderably in their combining weights. The same scale of ordinates is used for the two curves by plotting, instead of the amount of acid combined per gram by each protein at each pH, the fractions of the total amounts of acid which are required to bring them from a condition of equilibrium with a solution at pH 6.4 to one at pH 1 (the reason for choosing pH 6.4 will be apparent later). These curves are typical of those obtained over this range of pH with proteins of the two classes, and illustrate: (1) the long region, starting below pH 5 (and extending to pH 10) in which practically no acid combines with wool; (2) the much greater steepness of the curve for wool; and (3) the much greater acidity at which half the maximum amount of acid is combined.

Cannan has shown that this portion of the curve for *egg albumin* (after correction for the small amount of acid combination due to histidine) is readily described in terms of the law of mass action, using only a single dissociation constant, if allowance is made, in a semiempirical way, for the effect of electrostatic interaction between the ionized carboxyl groups on their respective dissociations [4]. Clearly, if a similar analysis is to be applied to the data for wool,

[5] The position and form of the acid titration curves are determined by the carboxyl groups of the protein rather than by the amino groups, because the latter are present as internally ionized ammonium-like salts. Thus the process of acid combination consists in replacing a proton on an ionized carboxyl group. The maximum amount of acid combined is, of course, determined by the number of amino groups [3, 7, 24].

additional factors must be taken into account. A possible clue to the nature of the difference is suggested by the fact that the steeper slope characterizing the curves for the insoluble proteins may be described to a good degree of approximation by substituting $(H^+)^2$ for (H^+) in the mass law expression for egg albumin used by Cannan.

It seems likely that these differences, characteristic not only of wool but of other high-molecular insoluble proteins as well [34], are necessarily associated with the presence of a separate phase. Nevertheless, many proteins which are relatively insoluble at their isoelectric points have hitherto been titrated in the presence of much undissolved material over at least part of the total range of the titration. Singularities and discontinuities, which may not be an essential part of the titration phenomena but rather the result of the disappearance or appearance of a second phase, have appeared in these data [5].

Among those who have recognized the existence of these differences between the titration curves of dissolved and undissolved proteins, Speakman and his collaborators [43, 44, 45] and Lloyd and Bidder [34], have preferred to attribute them to fundamental differences between the structures of insoluble and soluble proteins rather than to factors introduced by the existence of two-phase equilibria. Thus Speakman appears to believe that salt linkages, between acidic and basic groups, prevent the functioning of these groups in their customary ranges of acidity because certain minimal acid or base concentrations must be exceeded before such salt linkages are broken. This is equivalent to postulating a large charge effect, transmitted through the solvent medium, on the dissociations of these groups. In view of the high dielectric constant of water, the postulated magnitude of this effect is open to question [2]. In addition, Lloyd and Bidder, working with collagen, gelatin, silk, and horsehair, attribute a part of the inactivity of acidic and basic groups at reactions near neutrality to the existence of vaguely defined covalent linkages between adjacent polypeptide chains, which render the groups in question unavailable until these linkages are destroyed by exposure to sufficiently concentrated acid or alkali.

Nevertheless, all of these authors, and others who have been concerned with the electrochemical and osmotic behavior of insoluble proteins, have recognized that account must be taken of the presence of two phases, and have had recourse to the usual method of describing such phase equilibria by means of the Donnan equations [12, 13], at least in a qualitative way. A *quantitative* analysis of the titration curve, sufficient to decide the extent to which the existence of two phases eliminates the need to consider other factors of the kind mentioned above, has not hitherto been made. The reason for this is not far to seek: There are grave difficulties in defining, without arbitrariness, the compositions of the phases in applying the equations of the Donnan equilibrium to the cases in question. In the present paper new data on the combination of wool with both acid and base are described in terms of a more readily defined and simpler concept. This treatment does not pretend to supplant the treatment of Donnan in other cases of two-phase equilibrium for which exact information as to the composition of clearly delimited phases makes possible its proper application.

As a result of certain theoretical considerations,[6] it appeared likely that data obtained in the presence of neutral salt at constant ionic strength might shed light on the cause of the differences apparent between curves obtained with acid alone (fig. 1). The measurements to be described here, most of which were made at 0° C to avoid complications introduced by hydrolytic decomposition, have led to a simple and general way of relating these differences to the conditions under which insoluble proteins such as fibers must be titrated. It seems probable that the resulting viewpoint has consequences for many phenomena characteristic of soluble as well as of insoluble proteins. Thus, for example, in the study of the effect of pH upon protein solubility a condition necessary for measuring the phenomenon is the presence of the solid phase.

II. EXPERIMENTAL PROCEDURE

1. MATERIAL

Raw wool fibers were cut into root and tip portions, and the latter, which are contaminated and partially decomposed, were discarded. The root portion was purified by washing in cold ether, extracting for 16 hours, first with alcohol and then with ether, at temperatures below 35° C, and finally washing repeatedly in distilled water. It was carded by hand or on a sample carding machine,[7] rewashed in distilled water, air-dried, and finally conditioned at 21° C and 65-percent relative humidity before weighing. Analyses for total nitrogen, amide nitrogen, primary amino nitrogen, sulfur, and cystine gave nearly identical results with all the batches of wool used. Analyses for ash were made by combustion, and by an adaptation of the electrodialysis method of Joseph and Stadie [30, 48]. Most of the data on combination of acid at 0° C were obtained with wool containing only 0.10 percent of ash. No effort was made to remove this ash and no correction was applied for its effect (shown to be very small, see section III–1) on the amount of acid combined. The remaining data, obtained with material of higher ash content (0.26 percent), were corrected for the alkali equivalence of the ash by subtracting from or adding to the measured acid- or base-binding capacity an amount determined by direct comparison with the low-ash wool, occasionally supplemented by other methods of estimation.[8] The moisture content of the fibers used in each experiment was determined by drying representative samples for 2 hours in a vacuum oven at 105° C. The data are expressed as acid or base bound per gram of dry wool.

2. METHODS

(a) TITRATION WITH ACID

Samples of wool weighing either 1.2 or 2.0 g and containing from 13.1 to 15.0 percent of moisture, were placed in 100-ml portions of acid solutions at the temperature of the experiment (0° or 25° C). The solutions contained varying amounts of hydrochloric acid and sufficient potassium chloride to bring them, after absorption of acid by

[6] These considerations are discussed in section IV.

[7] Thanks are due to the Eavenson and Levering Co., of Camden, N. J., for carding four batches of wool used in this work.

[8] The principal alternative method used was an electrodialytic estimation of combined base, by an adaptation of the method of Joseph and Stadie [30].

the fibers, to predetermined ionic strengths between 0.005 and 1.0. Sets of solutions containing only HCl, without added salt, were also used. Rapid and complete wetting-out of the wool was facilitated by pumping off air with a filter pump. Repeated preliminary sampling showed that during immersion over a period of 48 hours at the lower temperature, there was a perceptible drift of pH in solutions from which a large fraction of the total acid was removed by combining with the wool. Therefore, in order to assure attainment of equilibrium, the fibers were exposed to the solutions at either temperature for periods of from 48 to 75 hours before samples were withdrawn. Portions of each solution, transferred to stoppered Pyrex test tubes, were allowed to come to room temperature (22° to 31° C) and the pH of each was determined. Aliquots of the original solution and of the solution in equilibrium with the wool were titrated with sodium hydroxide, using bromcresol purple as indicator. From the difference between these titers, the weight of the sample, and its content of moisture, the amount of acid taken up per gram of dry wool was calculated. Since differences in titers are involved, and since these differences do not change in direct proportion to the total concentration of acid, the measurements made in the most acid solutions are most subject to error. This limitation of accuracy was partly offset by using the larger wool samples in the most acid solutions.

The chloride disappearing from solution was determined by titrating the same aliquots, after neutralization, with 0.1 *M* silver nitrate. Sufficient potassium chromate solution to bring the chromate concentration above 0.01 *M* was used as indicator. Errors caused by end point uncertainties were reduced by matching the colors of the aliquots with one another.

In calculating the hydrogen ion and chloride ion bound by the fibers from the difference in titers of the solutions, proper account was taken of the effect of water absorption by the fibers on the final concentration of acid. With the ratios of fibers to solutions used, this correction was negligible except when the acid concentration exceeded 0.1 *M*, but the importance of this procedure has been amply demonstrated by critical experiments with ratios more favorable to the detection of effects due to moisture absorption. In calculating these small corrections, it has been assumed that the hydration of the fiber is the same in acid solutions as it is in water, and that no hydrochloric acid is dissolved in the water taken up. Recent unpublished measurements on cotton fibers in this laboratory indicate that the latter assumption may not be strictly true, but only a slight over-correction results from its use. Omission of the correction would result in an apparent decrease in the acid bound when the concentrations of acid exceeded 0.2 *M*.

In order to determine whether prolonged exposure to acid produced significant hydrolysis of amide bonds, other aliquots from each solution were tested for ammonia with the Nessler reagent of Koch and McMeekin [33]. At 0° C, only the highest acidities used (over 0.2 *M*) produced a detectable amount of ammonia (0.06 mg/g). The effect of this amount on the titration curve is practically negligible. At 25° C, concentrations over 0.1 *M* produced sufficient ammonia to account for 0.01 to 0.03 millimole of acid combined. This is equivalent to hydrolyzing from 1 to 2 percent of the amide groups present. Tests

with the phenol reagent of Folin and Ciocalteu [14] showed the presence of traces of a reducing substance in the most strongly acid solutions. This appeared to be present in the wool before treatment with acid rather than to result from decomposition, since the maximum amount found was the same at both temperatures. Negative sulfide and biuret tests on the solutions showed that no appreciable dissolution or decomposition had occurred.

(b) TITRATION WITH BASE

Portions of wool weighing either 3.0 or 4.0 g were placed in carbonate-free alkaline solutions (usually in volumes of 200 ml) at 0° C. The solutions contained varying amounts of potassium hydroxide and sufficient potassium chloride to bring the total ionic strengths to predetermined values of 0.02 or 0.2 *M*. Sets of solutions without added salt were also used. The larger samples were used in the most alkaline solutions. Although it is very desirable to limit the time of exposure to alkali to a minimum in order to minimize the amount of decomposition, control experiments at acidities at which decomposition was negligibly slow showed that periods of immersion of at least 18 hours were required to attain equilibrium. Approximately 20 hours was allowed in all the experiments reported, with the exception of those mentioned later.

In determining the amounts of base bound, the procedure of Harris and Rutherford [25] was followed except for the substitution of bromcresol purple for methyl red as indicator, and the use of nesslerization for the determination of dissolved protein. Additional aliquots were used for immediate measurement of pH at the temperature of the experiment. The use of bromcresol purple reduced the error introduced on the acid side of pH 6 by the buffering capacity of dissolved protein in those solutions in which appreciable decomposition has occurred.[9]

A slight modification of the method of calculating the corrections for decomposition was introduced. Comparisons of the ratio of dissolved nitrogen, after Kjeldahl digestion, to dissolved inorganic sulfur with the same ratio in the intact protein indicated that a small fraction (usually from one-tenth to one-fifth) of the inorganic sulfur in each solution was derived from the wool that had dissolved. Therefore, only the remaining eight- or nine-tenths of the inorganic sulfur in solution was produced by hydrolysis of disulfide bonds *in the undissolved wool*. Only the latter portion should be included in the correction for disulfide bonds broken since the base taken up by the dissolved protein, including that taken up by the sulfhydryl groups formed by hydrolysis of its own cystine, is not measured by the differential titration method used in this work.

This modified correction was shown to be justified by control measurements with several different concentrations of potassium hydroxide between 0.05 and 0.30 *M*, and with periods of immersion between 1.5 and 27 hours at 0° C. These measurements showed that with the highest concentrations there is a measurable increase in the amounts of base combined up to at least 10 hours, and that after this period,

[9] Buffering capacity on the alkaline side of the pH for zero combination is taken care of by the method of correction for the effects of decomposition used by these authors.

the amount bound does not change if the constantly increasing corrections for decomposition are properly made. If, on the other hand, the corrections are applied as in the method of Harris and Rutherford, the calculated amount of base bound decreases somewhat on prolonged exposure to strongly alkaline solutions. This would be the expected result of over-correction when the amounts of decomposition become large. The same effect is evident when results at different concentrations of potassium hydroxide, obtained after the same times of exposure, are compared. The calculated amounts of base bound tend to *decrease* at the highest concentrations, if the correction for *all* the inorganic sulfur is applied.

At 0°C the largest correction, 0.28 milliequivalent per gram, (M-eq/g), corresponded to the destruction of approximately one-half of the disulfide bonds and the dissolving of one-twelfth of the total protein. In similar controls carried out at 25°C, as much as 85 percent of the cystine was destroyed, and up to one-sixth of the protein dissolved. With these larger amounts of decomposition, the necessity for modification of the method of Harris and Rutherford was even clearer. Thus, while the modification described here gave consistent results at the two temperatures, the unmodified corrections gave lower values at high concentrations of potassium hydroxide at the higher temperature.

Since the earlier measurements of Harris and Rutherford were obtained, for the most part, after exposure of wool to alkali for 2 hours, and since the corrections subtracted were slightly high, their values for the amounts of base bound are probably a little lower than the true equilibrium values. The data of the present investigation indicate that the maximum possible amount of base has not been bound even at potassium hydroxide concentrations of 0.3 *M*. However, the protein may be modified by decomposition of bonds other than disulfide when these or higher concentrations of alkali are used, and the methods of correction applied here may no longer suffice.

In view of the magnitude of the corrections described, no additional corrections for the effect of water absorption by the fibers on the calculated amount of combined base were applied. The small effect of this correction is within the error of the values given.

(c) MEASUREMENT OF pH

Measurements of pH were made with the glass-electrode assembly developed by MacInnes and Belcher [35], connected with a thermionic potentiometer which employed a cathode-ray "eye" as null indicator. The potentiometer, arranged to read directly in pH at temperatures between 0° and 30°C, could be set reproducibly to 0.002 pH unit when measuring buffered solutions. The following solutions [29] were employed in establishing the pH scale, in terms of which the measurements at 25°C are expressed: (a) 0.1 *M* hydrochloric acid; (b) 0.01 *M* hydrochloric acid plus 0.09 *M* potassium chloride, using the values 1.085 and 2.078; (c) 0.05 *M* potassium hydrogen phthalate,

using the value 4.008; (d) 0.1 *M* acetic acid plus 0.1 *M* sodium acetate, using the value 4.648; and (e) 0.05 *M* sodium tetraborate, with the pH value 9.180. In addition, 0.05 *M* potassium hydroxide was used. A pH of 12.61 was assigned to this solution, consistent with the activity coefficient (0.824) determined by Harned and Cook [20] and the value of Harned and Hamer [22] for the ion product of water ($pK_w = 13.997$).

Calibration at 0° C was carried out with the same solutions, omitting the sodium tetraborate. The same pH values were assigned to the hydrochloric acid and phthalate [18] solutions at both temperatures, but the value assigned to the acetate buffer at 0° C (4.673) was estimated by adding to the value at 25° C the logarithm of the ratio of the dissociation constants at the two temperatures. The negligible effect of temperature on the activity coefficients of the ions in these solutions is thus not taken into account in the values assigned. The pH assigned to 0.05 *M* potassium hydroxide at 0° C was 13.56, estimated from the value of Harned and Hamer at this temperature for pK_w (14.94) and the activity coefficient (0.829) determined by Harned and Cook.

When the pH-meter was set at the proper pH with any of these standards except the most alkaline one, each of the other four buffers could be read to within 0.01 pH unit of the values assigned to them. Readings in alkaline solutions required adjustment for the departure, at pH greater than 9, of the slope of the pH-emf function from its theoretical value. This adjustment was carried out as follows: After setting the pH-meter to read 4.008 with the phthalate buffer in the electrode vessel, the pH reading of 0.05 *M* potassium hydroxide was determined, and subtracted from the calculated correct reading. The difference (never over 0.26 pH unit at 0° C) was assumed to be uniformly cumulative over the pH interval of 8.55 units. This is equivalent to assuming that over this range of pH the proportionality between emf and pH is lower than the proper value of RT/F by about 3 percent. This assumption leads to adjustments which are subject to most error at pH 7 to pH 10. In this interval only a few readings were taken; and owing to the relatively small slope of this part of the titration curve, a small error in pH has very little effect on its shape or position. The pH values reported for alkaline solutions are less certain than those in the acid range because of these adjustments (based in part on a *calculated* pH), and because of some hysteresis of the glass membrane after exposure to concentrated alkali. The latter sometimes introduced a discrepancy of 0.03 to 0.04 pH unit, apparent when the measurements of acid standards were repeated after an alkaline series. In agreement with the work of Dole and Wiener [11], the required adjustments and the residual uncertainties are larger at the higher temperature.

The pH values of alkaline solutions were measured with the electrode assembly mounted in an air thermostat at either 3°C or 25°C. Solutions were introduced and manipulations made from the outside. The results given at 0°C are calculated from measurements made at

the lower temperature. Practically all acid solutions were measured at room temperature. Since many of the solutions were very poorly buffered, the accuracy of a large number of the measured pH values was tested by direct comparison with the calculated values based on the titer of the solutions and the activity coefficients of the acid or base [19, 20, 21, 22, 26]. With solutions more acid than pH 3.5 at ionic strengths below 0.1 *M*, agreement to 0.01 pH unit was usually found. The presence of *traces* of a soluble buffering substance derived from the wool reduced this agreement in the range pH 4 to pH 10, but in the absence of wool this agreement extended to pH 4.5, beyond which the concentration of HCl could not be accurately determined. The stability and reproducibility of the measurements below pH 6 render it very probable that the same high accuracy prevails up to this value, even in the presence of wool. Measurements between pH 6 and pH 9 required almost continuous flushing of the electrode vessel, and are less certain. pH values for solutions containing potassium hydroxide in concentrations of 0.1 *M* or more were calculated from their titers, allowance being made for the contribution to the titer of any hydrosulfide present. Acid solutions with an ionic strength of more than 0.1 required application of a small empirical correction (between 0.02 pH at ionic strength 0.2 and 0.11 pH at ionic strength 1.0) due to the difference in ionic strength between the standardizing buffers and the solutions measured.

(d) CONTROL OF TEMPERATURE

A well-stirred 200-liter water-thermostat equipped with cooling coils, 300-watt heating element, mercury thermoregulator, and time-delay relay, kept the temperature constant at 25.00°±.02°C. No thermoregulator was used at 0°C; ice was allowed to form on the coils as the result of intermittent operation of the cooling unit. With a large amount of ice present, the temperature remained constant to ±0.01°C.

III. RESULTS AND DISCUSSION

1. COMBINATION WITH HYDROCHLORIC ACID

Measurements of the combination of wool with hydrochloric acid as a function of pH at 0°C are given in table 1, in which each section, except the first, summarizes data obtained at a different constant ionic strength. In the first section, each measurement represents a different ionic strength, since no salt was added. Data obtained both by titration of acid and of chloride are given. As was to be expected from considerations of electrical neutrality, the values in the two columns agree very closely. This agreement shows that the small amount of alkaline ash in the material used in most of the experiments neutralizes only negligible amounts of acid. In those cases in which much ash was known to be present, the agreement demonstrates the adequacy of the corrections applied for the effect of this ash.[10]

[10] When alkaline ash is combined with wool, the chloride disappearing from solution rather than the decrease in titratable acidity is a measure of the acid which would be taken up by ash-free wool. Thus, curves of chloride bound as a function of pH, although of lower accuracy, require no adjustments for the presence of ash.

TABLE 1.—*Combination of wool with* HCl *at 0° C*

pH	Acid bound	Chloride bound
	Millimoles/g	*Millimoles/g*
(a) No added salt		
0.447[a]	0.868	
0.635	.838	
0.792[a]	.836	0.810
0.813	.805	.804
0.814[a]	.829	.836
0.918[a]	.813	
1.087[a]	.762	.771
1.125	.789	.736
1.470	.768	.754
1.663[a]	.676	.694
1.711	.652	.654
1.741[a]	.631	.635
1.931	.574	.585
2.061[a]	.510	.515
2.228	.445	.440
2.340[a]	.385	.399
2.451	.348	.353
2.726	.251	.261
3.039	.166	.169
3.272	.114	.113
3.620	.067	.071
3.844	.045	
4.198	.027	.023
4.414	.017	.023
4.740	.012	.018
5.145	.004	.009
(b) Ionic strength 0.005		
2.340	0.385	0.399
2.681	.314	.324
2.980	.264	.263
3.469	.187	.193
3.778	.146	.143
4.130	.113	
4.403	.085	.088
4.701	.058	.073
5.108	.045	.046
5.236	.035	.039
5.670	.022	.024
5.769	.021	.019
5.90	.009	
6.5	.000	
(c) Ionic strength 0.01		
2.061	0.510	0.515
2.442	.427	.427
2.705	.369	.368
2.982	.312	.312
3.326	.250	.266
3.593	.209	.221
3.856	.167	.167
4.412	.113	.118
4.652	.089	.095
5.072	.061	.079
5.317	.050	.059
5.649	.032	.043
5.98	.017	.021
6.41	.008	
6.5	.000	

pH	Acid bound	Chloride bound
	Millimoles/g	*Millimoles/g*
(d) Ionic strength 0.02		
1.741	0.631	0.635
1.950	.591	.621
2.265	.525	.525
2.675	.429	.429
3.017	.365	.366
3.368	.289	.295
3.668	.240	.238
3.945	.202	.204
4.563	.121	.118
5.048	.074	.080
5.622	.042	.047
6.4	.000	
(e) Ionic strength 0.04		
1.663	0.676	0.694
1.830	.668	.675
1.925	.650	.678
2.152	.605	.616
2.620	.505	.494
2.639	.500	.494
3.016	.406	.400
3.294	.357	.382
3.628	.280	.319
4.035	.229	.222
4.377	.171	.193
4.650	.146	.140
5.080	.102	.102
5.283	.082	.082
5.40	.064	.063
6.3	.000	−.011
(f) Ionic strength 0.1		
1.087	0.762	0.771
1.201	.789	.794
1.380	.767	.776
1.678	.745	.740
1.988	.704	
2.269	.664	.680
2.535	.603	
2.810	.538	.510
3.206	.446	
3.650	.357	
4.210	.250	
4.617	.176	.195
5.032	.122	
5.473	.075	
5.867	.037	
6.15	.016	
6.3	.008	
6.4	.003	
6.5	.000	
(g) Ionic strength 0.2		
0.792	0.836	0.810
0.814[b]	.829	.836
0.918[a]	.813	
1.100	.799	.788
1.130[a]	.798	.828
1.400[a]	.789	

See footnotes at end of table.

TABLE 1.—*Combination of wool with* HCl *at 0° C*—Continued

pH	Acid bound	Chloride bound
(g) Ionic strength 0.2—Continued		
	Millimoles/g	*Millimoles/g*
1.409	0.788	0.773
1.433[c]	.774	.780
1.707	.770	.756
1.751[c]	.753	.775
1.982[b]	.730	.730
2.038	.740	.756
2.061[c]	.702	.759
2.364	.701	.712
2.378[c]	.670	
2.708	.641	
2.744[c]	.595	
2.790[d]	.594	
3.172	.535	.591
3.273[c]	.487	
3.571[b]	.435	
3.670	.419	.460
3.825[c]	.372	
4.082	.320	.294
4.359[b]	.279	.300
4.662	.224	.198
4.855[c]	.177	
5.015	.168	
5.246	.131	.120
5.400[c]	.112	
5.528	.099	.085
5.564[c]	.067	
5.670	.078	
5.887	.054	
5.94[c]	.030	
6.14	.023	
6.3[c]	.002	
6.5	.002	
6.7[c]	−.027	
6.97	−.048	
7.0[c]	−.041	

pH	Acid bound	Chloride bound
(h) Ionic strength 0.5		
	Millimoles/g	
0.447	0.868	
0.832	.838	
1.130	.850	
1.438	.799	
1.745	.784	
2.048	.781	
2.780	.687	
3.750	.471	
3.910	.432	
4.304	.330	
4.887	.228	
5.211	.164	
5.472	.112	
5.870	.068	
6.10	.034	
6.5	.002	
(i) Ionic strength 1.0[a]		
0.578	0.920	
0.840	.890	
1.138	.852	
1.445	.840	
1.743	.794	
2.062	.777	
3.074	.652	
4.258	.403	
4.334	.395	
4.768	.288	
5.342	.208	
5.651	.119	
5.908	.065	
6.4	.013	
6.7	−.015	
7.0	−.048	

[a] No-salt data from experiments at constant ionic strengths in other columns.
[b], [c], [d] Supplementary control determinations on three different batches containing alkaline ash. These data are corrected for differences in ash as explained in the text.
[e] Data in this column corrected for alkaline ash of wool used.

The measurements of acid bound (table 1) are represented graphically in figure 2, in which the continuous curves serve to differentiate the sets of points from one another. All of the other curves shown are distinguished from the "no-salt" curve (at the extreme left of the figure) by their smaller slopes. When compared at a point well above the base line, as, for example, at the points at which half the maximum acid-binding capacity is found, the slopes of all of them are very nearly equal. Near the base line the slopes vary as the curves converge and finally cross.[11] The addition of even small amounts of salt suffices to produce this difference: thus, when compared at 0.05 millimole of acid bound per gram, the point on the curve obtained with a total ion concentration of only 0.005 is shifted with respect to a corresponding point on the no-salt curve by about 1.3 pH units. The magnitude of this effect may be made clearer by comparing the amounts of acid bound at the same pH. In the absence of salt, only a little more than 0.01 millimole of acid per gram is bound at pH 4.6, but the addition of salt, sufficient to bring the concentration of chloride to 0.005 *M*, increases this figure almost sixfold. At pH 5 and above, this factor is even larger. Conversely, as the part of the total ionic strength which

[11] The positions of the curves are reversed on the alkaline side of the point of zero combination and again tend to become parallel.

is contributed by salt diminishes, the factor becomes smaller, and each curve finally terminates at its intersection with the curve obtained without salt.

A simple regularity relates the curves obtained with different total ionic strengths: the distance (with respect to pH) between any two adjacent curves, taken for convenience at the point of half of the maximum combination with acid, is only slightly less than the logarithm of the ratio of the ion concentrations which the curves represent.

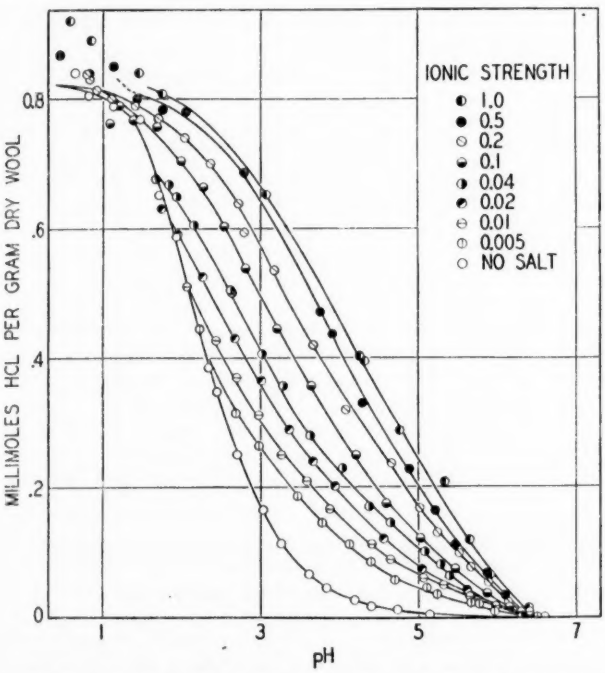

FIGURE 2.—*Combination of acid by wool as a function of* pH *and ionic strength at* 0° *C.*

(To avoid crowding the figure, only a single set of the experimental values obtained at an ionic strength of 0.2 is included. The smooth curves serve merely to distinguish the sets of data from one another.)

This implies a close approach to a direct stoichiometric relationship of the acid bound by wool to the concentration of chloride ion as well as to the concentration of hydrogen ion: Thus each time the chloride concentration is doubled, the curves are shifted to pH values approximately 0.30 unit higher than those at the lower ionic strength. As shown in figure 3, this direct relation is approximated very closely over the fortyfold range of chloride concentrations between 0.005 and 0.200 *M*. Above this range the dependence on ionic strength diminishes: It appears that the curves may approach a limiting position with respect to the pH axis, and that this limit may not be far beyond the position of the curve at 1.0 *M* ionic strength. It is significant that the pH for half maximal combination (4.2) which characterizes the position of the curve at 1.0 *M* chloride is practically identical with

the midpoint of the first S-shaped portion of the titration curves of soluble proteins measured at the same salt concentration.

The remarkably regular dependence of the positions of the curves on the total concentration of chloride ions may be interpreted as implying a certain degree of interchangeability of the concentrations of acid and salt or of hydrogen and chloride ions as factors limiting the amounts of acid bound. The function which describes the amount of acid bound must involve two independent variables, and its dependence on each of these variables must possess a degree of similarity.

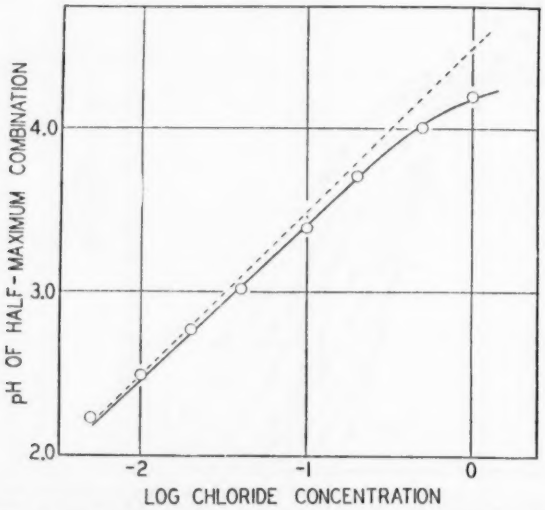

FIGURE 3.—*The dependence of the* pH *of half-maximal combination with acid on the level at which the chloride concentration is held constant.*

The broken line represents a direct stoichiometric relation.

Thus, if, instead of plotting the amount of acid bound against pH it were plotted against the negative logarithm of the total chloride concentration at a number of constant concentrations of acid, a group of curves would be obtained related to one another very much as the curves in figure 2. Several earlier studies on *soluble* proteins [4, 10] have shown the existence of much smaller effects of salt on the positions and shapes of their acid-titration curves. These effects are only slightly larger than those which characterize the common buffers, and which are explained in terms of the modern electrical-interaction theory of solutions. They cannot be compared to the much larger and nearly stoichiometric dependence which is found with wool in the range of low ionic strengths. The significance of this large and interchangeable dependence of acid and salt on acid combination is discussed in section IV of this paper.

Since the curves of acid combination as a function of pH represent the reaction of hydrogen ions with carboxylate ions (see footnote 5), and since the dissociation constants of the conjugate carboxylic acids have only a slight dependence upon temperature (between 0° C and room temperature), the effect of temperature on these curves should be small. This expectation is completely fulfilled by comparison of

the data at 0° already given with the measurements on wool at 25° C summarized in table 4 and plotted in figures 1 and 5.[12] Comparison of the data obtained in the absence of salt at either temperature with the data of Speakman and Stott [45], obtained at an intermediate temperature, is therefore not unjustified. The agreement with the data of these investigators is close over the greater part of their range, and is probably within the limits of possible differences in definition of the pH scale in the two investigations. Although different wools were used, there is also close agreement between the values for maximum acid-binding capacity. As shown in figure 2, all of the sets of points tend to level off near pH 1 at 0.80 to 0.84 M-eq of acid bound per gram.[13] Speakman obtained a maximum of 0.80 or 0.81 with wool which had been previously extracted with very dilute hydrochloric acid to remove the ash. The agreement of our maximum values with his supports the previous conclusion that the residual 0.10 percent of ash in the wool used in the present investigation is practically without effect on the measurements. This conclusion is also borne out by the amounts of acid shown to be bound in the absence of salt at pH 4.8, which Speakman considers to be the point of zero combination. This quantity, approximately 0.01 millimole per gram, is therefore the maximum amount which may be attributed to ash present in the wool of the present investigation. The effect of this ash in neutralizing acid may be even smaller, or zero, since Speakman's acid extraction and adjustment to pH 4.8 may have resulted in the combination of so small an amount of acid as 0.01 millimole with his wool. The curves obtained in the presence of salt make plain that pH 4.8 is not the point of zero combination of acid with wool at 0° C. It seems probable that at this temperature the base line is crossed, not only in the presence of salt but in salt-free solutions as well, at pH 6.3–6.5.

2. COMBINATION WITH POTASSIUM HYDROXIDE

Although fewer measurements of the combination of wool with base have been made, they suffice to show that the relationships between the data on acid combination obtained in the presence and absence of salt, and at different constant ionic strengths, also prevail in the alkaline branches of the wool titration curves. Very little modification of the foregoing description is therefore necessary. The corrected data for base combination at 0° C, at two ionic strengths and in the absence of added salt, are summarized in table 2. Parallel data for the combination of the fiber with potassium ion, obtained by electrodialysis, are omitted from this table; although less accurate than the data for base bound, they are in fair agreement with the values given. In figure 4, the data of table 2 are shown combined with the corresponding sets of measurements for acid combination; the figure thus represents the complete titration curve under these conditions over the entire pH range studied.

[12] A closer study of the effects of temperature on the combination of acid and base is in progress. These effects are of importance in the application of the low-temperature titration data presented in this paper to such related aspects of wool processing as dyeing and scouring, which usually involve high temperatures.

[13] The slight differences in the maxima shown by the various curves may represent, in part, residual differences in alkaline ash for which inadequate corrections have been made. It is more likely that they are the result of incorrect allowance for differential absorption of water, salt, and acid when wool unsaturated with water is placed in the various solutions. This absorption will affect only the values calculated for the most acid solutions. It is also possible that in the most acid solutions, the titration of the very weakly basic amide groups is begun, and that the curves are not entirely level below pH 0.7.

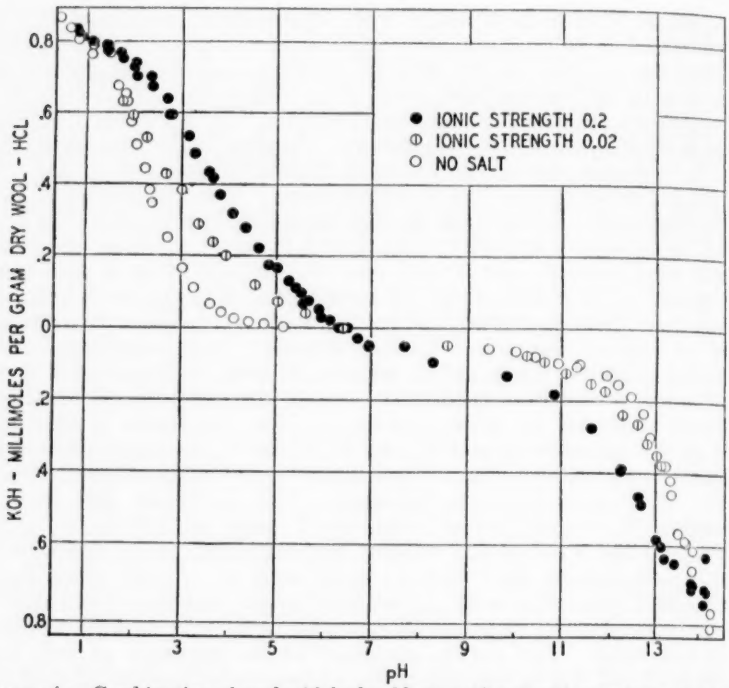

FIGURE 4.—*Combination of wool with hydrochloric acid and with potassium hydroxide as a function of* pH.

Data are shown obtained in the absence of added salt, and in the presence of two different constant total ionic concentrations.

TABLE 2.—*Combination of wool with* KOH *at 0° C* [a]

pH	Base bound	pH	Base bound	pH	Base bound
(a) No added salt		(b) Ionic strength 0.02		(c) Ionic strength 0.20	
	Millimoles/g		*Millimoles/g*		*Millimoles/g*
[b] 9.45	0.055	8.59	0.047	[e] 6.95	0.050
[b] 10.01	.063	10.25	.095	7.68	.050
[b] 10.43	.077	10.62	.112	8.28	.093
[b] 10.91	.094	11.09	.142	9.84	.130
11.32	.105	11.60	.170	10.83	.180
11.37	.097	11.90	.191	11.63	.273
11.93	.128	12.27	.236	[e] 12.23	.391
12.17	.153	12.60	.262	12.25	.389
12.46	.185	12.81	.316	12.62	.462
12.72	.232	13.03	.348	12.68	.495
12.88	.297	13.22	.397	13.01	.582
13.12	.375			[e] 13.11	.600
[e] 13.22	.397			13.19	.635
13.32	.436			[e] 13.39	.649
13.35	.476			[b] 13.82	.704
13.49	.565			[d] 13.82	.722
[b] 13.65	.586			[e] 13.85	.710
13.68	.590			[f] 14.11	.764
13.85	.669			[b] 14.13	.723
[b] 13.85	.611			[e] 14.16	.630
14.11	.764			[d] 14.17	.730
[b] 14.13	.723				
[e] 14.16	.630				
[d] 14.17	.730				
14.29	.828				
[b] 14.30	.787				

[a] The data are corrected for the effects of decomposition and for the content of alkaline ash, as explained in section II.

[b], [e] Supplementary control determinations on two different conditioning batches, and with different periods of equilibration.

[d] Control determinations on wool of different ash content.

[e] Data from section (b).

[f] Data from section (a).

When the data obtained at constant ionic strengths are so presented in their entirety, the composite curves bear a close resemblance to the titration curves of dissolved proteins. The acid branch crosses the base line without discontinuity and continues downward with progressively more gradual slope until buffering capacity is practically lost over a range of 1 to 2 pH units. Approximately 0.10 millimole of base per gram has been bound at this point. As the pH increases, marked buffering capacity once more appears and large amounts of base are bound in the pH range 11 to 14. The largest amount bound in the range measured is 0.78 millimole per gram, but there is no indication from the shape of the curves that somewhat larger amounts of base would not be bound at a higher pH. This maximum value is slightly higher than that reported by Harris and Rutherford. The cause of part of this difference has already been given (see section II). Another part may be due to the alkaline ash content of the wool yarn, as pointed out in the earlier work.

Although the alkali titration curve is more complex than the acid curve, the shifts produced in its position by salt are exactly analogous to the shifts in the acid curves. Thus every point on the curve representing measurements at 0.02 *M* is shifted to the alkaline side by almost exactly 1.0 pH unit from the corresponding point at 0.20 *M*. The data obtained without salt are widely separated from the others, especially as the pH for zero combination is approached. The curve representing the data obtained in the absence of salt in both alkaline and acid solutions consists of two steep sections and shows clearly the long central region of about 5 pH units in which the amounts of acid or base bound are very small.

3. RELATIONS TO TITRATION CURVES OF SOLUBLE PROTEINS

The occurrence of a large and nearly stoichiometric dependence of the pH coordinate of the titration data for wool on the ionic concentration makes it of some interest to determine whether any of the large number of possible positions of the resulting curves corresponds with the curve which would characterize a similar protein in the dissolved state. It has been shown (fig. 1) that the acid curves of wool and of a comparable soluble protein, egg albumin, obtained in the total absence of salt, differ very widely. In figure 5, data for the same two proteins are compared at a high salt concentration, 0.5 *M*. Above this concentration the positions of the titration curves with respect to the pH axis have a lower degree of dependence on salt concentration.[14]

The data for wool shown in figures 1 and 5 were obtained at 25° C, the temperature used by Cannan, and are summarized in table 3. The points for egg albumin in figure 5 represent interpolations at equidistant points along the pH axis between the curves given by Cannan [4] for 0.27 and 0.67 *M* salt. The data for wool at 25° C differ only slightly from those at 0° C already described.

It is clear that the differences between the data for the two proteins, so marked in figure 1, have been greatly reduced in figure 5. Aside from a slightly more acid position for the curve for wool, discrepancies to which significance may be attached appear only in the region of very slight acid binding. These discrepancies are very small. Some disagreement might be expected in this region owing to small dif-

[14] The smaller shifts that occur at salt concentrations above 0.5 *M* are of practically the same magnitude as those which occur with the dissolved protein in the same range of concentrations.

ferences between the ratios of imidazole to carboxyl groups in the two proteins. Since the histidine content of both proteins is small, it is very likely that the analytical values reported are not exact.

TABLE 3.—*Combination of wool with hydrochloric acid at 25° C* [a]

(a) No added salt		(b) Ionic strength 0.59	
pH	Acid bound	pH	Acid bound
	Millimoles/g		*Millimoles/g*
0.638	0.877	0.412	0.877
0.826	.802	0.839	.810
1.448	.687	1.154	.815
1.710	.599	1.470	.824
1.915	.520	1.774	.757
2.191	.402	2.088	.762
2.406	.316	2.835	.636
2.722	.225	3.772	.426
3.093	.143	3.929	.383
3.370	.087	4.380	.281
3.962	.036	4.852	.214
4.603	.014	5.33	.140
5.257	[b]−.013	5.82	.082
6.38	[b]−.026	6.25	.023
6.82	[b]−.035	6.50	.002
7.28	[b]−.042	6.72	[b]−.026

[a] The data are corrected for water uptake by the fiber and the effect of its alkaline ash, as explained in section II.
[b] Negative values indicate loss of bound acid or combination with hydroxyl ion.

This comparison shows that proteins of comparable composition with respect to dicarboxylic amino acids and histidine, give closely similar acid-combination curves when they are compared over the same acid range in solutions containing high concentrations of ions. This

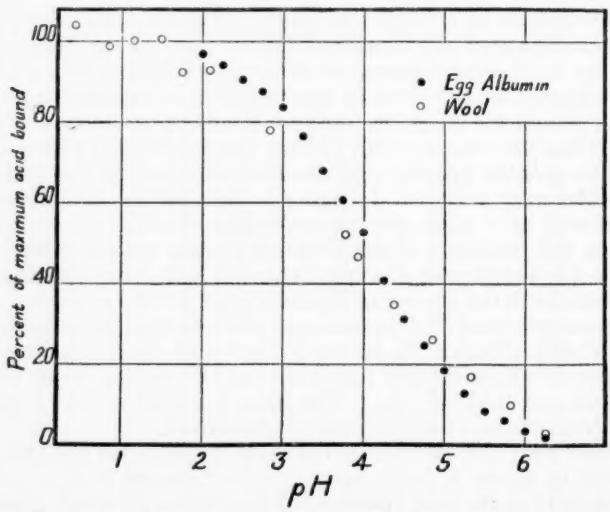

FIGURE 5.—*Comparison of the curves of acid combination of wool and of egg albumin at 25° C, in the presence of 0.5 M chloride.*

result must be taken into account in any explanation offered for the great difference in acid-binding behavior between the same proteins when neutral salts are absent. In itself, the comparison is sufficient

to exclude from consideration explanations which appeal to a fundamental difference in configuration of the acidic and basic groups in the two classes of substances. The comparison gains further significance from Cannan's demonstration that the egg albumin curves of figures 1 and 5 are very similar to those of polyvalent acids in which all of the dissociating groups have the same intrinsic strength, but in which the negative charges left by the dissociation of each hydrogen ion hinder the dissociation of the remaining groups. The present comparison indicates that Cannan's reasoning must apply to wool to the same degree as to egg albumin. The differences between the titration curves of the two proteins found in the absence of salt must find their explanation in elements of an equilibrium which occurs between two phases.

4. ANALYSIS OF THE TITRATION CURVES

By analogy with similar analyses of titration curves of soluble proteins [8, 9, 10, 27, 28], it should be possible to identify each portion of the curves for wool at high constant ionic strength with one of the several kinds of dissociating groups contributed by the constituent amino-acid residues. The acid branch is clearly attributable to the back-titrations of the ionized carboxyl groups of glutamic, hydroxyglutamic, and aspartic acids, overlapping in the pH range above 4.5 the combination with acid of the imino groups of histidine. In addition, those carboxyl groups which have not donated their protons to amino and guanidino groups (the excess of carboxyl groups over these groups) must be responsible for part of the unbroken continuation of this S-shaped curve to pH 8; another part is contributed by the removal of protons from those histidine residues which have their imino groups in the charged (acid) form. In the unbuffered region between pH 8 and pH 10 almost no groups dissociate, but in the buffered section of the curve (pH 11 to pH 14) the ϵ-amino groups of lysine are regenerated from their conjugate acid forms by loss of a proton. In addition, the hydroxyl groups of tyrosine (if they are free in wool) become ionized, and at least some of the guanidino groups of arginine, present in their conjugate acid form, give up their protons.

The foregoing partial analysis of the composition of the high ionic-strength curves may be rendered more convincing by the following quantitative comparison of its implications with the admittedly incomplete data at present available on the amino-acid composition of wool.

TABLE 4.—*Acidic and basic amino-acids in wool*

	Reference	Percent	Millimoles per gram
(1) Aspartic acid	[46]	7.27	0.545
(2) Glutamic acid	[46]	15.27	1.035
(3) Amide nitrogen	[46]	1.37	0.978
(1) plus (2) minus (3)			0.602
(4) Arginine	[16]	10.2	0.586
(5) Lysine	[39]	3.3	.226
(6) Histidine	[50]	0.66	.044
(4) plus (5) plus (6)			0.856
(1) plus (2) minus (3) plus (4) plus (5) plus (6)			1.458
(7) Tyrosine	[38]	5.8	0.320

The sum of the acid-binding and base-binding capacities of wool between pH 0.8 and pH 14.3 is 1.59 ±0.04 millimoles per gram. Table 4 lists the reported contents of aspartic and glutamic acids, histidine, lysine, arginine, amide nitrogen, and tyrosine. The sum of the acid- and base-binding equivalents, *omitting the tyrosine*, and after subtraction of the amide nitrogen to allow for the part of the dicarboxylic acids present as glutamine and asparagine, is 1.46 millimoles per gram. *With the tyrosine included* it is 1.78. Both figures are given because the experimental sum falls between them, and because there is a suggestion in certain unpublished data on wool and in published data on some soluble proteins [15, 47] that some or all of the hydroxyl groups of tyrosine in proteins may not be free to combine with base. Another explanation of the small discrepancy is possible: The figures for the carboxylic acids and histidine were obtained by isolation methods and are likely to be low. Should this be the case one may conclude that tyrosine hydroxyl groups are *not* titrated. However, it is not certain that the present measurements give the maximum base-binding capacity, and only part of the arginine may be combined with base at pH 14.3. Should this be true one may conclude that the tyrosine is titrated quantitatively.

It is possible to calculate roughly what the maximum base-binding capacity should be from the maximum amount of acid which is bound and the pH at which no combination with either acid or base occurs. Since the latter falls in the titration range of histidine, which is present in small amount, it appears that in the uncombined state of the protein practically all the carboxyl groups have donated their hydrogen ions to basic groups. Thus the sum of the basic groups (from lysine and arginine) must be equal to the sum of the carboxyl groups (from glutamic, hydroxyglutamic, and aspartic acids) within a margin of uncertainty which is smaller than the small content of histidine. The maximum base-binding capacity, *excluding tyrosine*, should therefore correspond roughly with the maximum acid-binding capacity,—which may be taken as 0.82. The sum of the two should not be far from $2\times0.82=1.64$, a figure close to 1.59, the value found. It would be necessary to assume that about half the arginine is still not titrated at pH 14.3 in order to make room for the titration of all the tyrosine. This would increase the maximum amount of base bound at higher alkalinities to about 1.18, far above the figure found at pH 14.3. The balance of probability therefore favors the conclusion that in the unhydrolyzed wool the hydroxyl groups of tyrosine are not free to combine with base, and therefore contribute no part of the large buffering effect at pH 11 to pH 14.

This conclusion entails the plausible assumption that some or all of the analytical data are low. Since the sum of the arginine and lysine listed in the table is 0.82 millimole per gram, in good agreement with the capacity of wool to bind acid, the largest part of the discrepancy must be sought in the values for the dicarboxylic acids and amide nitrogen, in both of which the potentialities for error have long been recognized. The relatively large amount of acid plus base combined between pH 6 and pH 8 (about 0.13 millimole) suggests that the histidine figure in table 3 may also be low, since only a small part of the combination in this range may be attributed to carboxyl groups. However, an increase in the estimated histidine content will not greatly affect the close agreement of the experimentally

determined sum of acid- plus base-binding capacity with the sum calculated from the acid-binding capacity alone, since only an indeterminate part of the histidine content contributes to the curve of acid combination, the balance being responsible for a part of the base combined at higher pH.

This analysis of the structure of the titration curve of wool differs in at least one significant respect from the interpretation offered by MacMahon and Speakman [36]. These authors regard the step on the curve which represents the base bound in salt-free solutions, between the pH at zero combination and the relatively unbuffered section at pH 8 to pH 10 as caused by the titration of sulfhydryl groups which are present in wool that has suffered partial decomposition. In the present investigation on undamaged wool, this step on the curve of base combination also appears; in the curves obtained in the presence of salt it clearly represents a continuation of the first S-shaped branch of the titration curve which begins its downward course near pH 1, and which has been accounted for above as an expression of the partially overlapping titration of carboxyl and imino groups. It seems unlikely that sulfhydryl groups, which are extremely weak acids, would be appreciably titrated in this range of pH. The formation of strongly acid groups by exposure to light may result in a shift of the pH at zero combination to lower values. This would have the effect of increasing the height of the alkaline step, which Speakman attributed to sulfhydryl.

IV. THEORY OF THE COMBINATION WITH ACID[15]

1. COMBINATION OF INSOLUBLE AMPHOLYTES WITH THE ANIONS OF ACIDS

It has been shown in a previous section (III–1) that the acid bound by wool is a function of the concentration of salt as well as of the concentration of hydrogen ions. Furthermore, the way in which the total anion concentration (from acid plus salt) participates in any equation defining the amounts of acid bound under various conditions must be in some measure analogous to the manner of participation of the hydrogen ion. When it is considered that practically equivalent quantities of hydrogen and chloride ions must be combined, dissolved, or adsorbed by the fiber, it is evident that the extent to which one of these ions may be taken up depends in part on the simultaneous availability of ions of the opposite sign.

Restrictions of the latter kind in two-phase acid-base equilibria have long been known. Cases involving two sharply delimited phases, separated by a membrane which is impermeable to one or more of the ions present, have been treated thermodynamically by Donnan [12, 13]. Application of the Donnan equations to the present case would involve elements of arbitrariness in the choice of volumes, concentrations, concentration-scale (because of the high concentration of dissolved substances), the distinction between acid bound by protein and acid merely dissolved by the medium present in the fiber phase, and in the allocation of the phase boundary. It will be shown later that with such an arbitrary choice permitted, a

[15] The acid branch of the titration curve has been chosen for discussion because it is composed of fewer distinct components. The treatment here proposed should be applicable, with suitable modifications, to the alkali branch as well.

good approximation to certain features of the data already described could be made. In other respects the approximation is less successful, and leads to consequences which appear to be incompatible with the comparison made above between data for wool and for soluble proteins. For these reasons, and because of the nearly complete interchangeability of hydrogen and chloride ions suggested by our results in acid solutions, it has seemed preferable to treat the restriction on the combination of wool with hydrogen ions more simply on the basis of three easily stated assumptions:

1. *The fiber protein combines with chloride ions as well as with hydrogen ions, and the combination of both is subject to the law of mass action, or to the Langmuir adsorption law.*[16] This assumption may be thought of as implying the formation of a partially dissociated linkage between RNH_3^+ groups and Cl— ions. Alternatively, the positively charged acid fiber might be thought of as forming a unimolecular adsorption layer of chloride ions. However, the observation that acid-dye anions permeate a wool fiber with a high degree of uniformity when time for full penetration is allowed shows that if the latter view be taken, adsorption does not occur merely on the outside of the fiber. The existence of stoichiometrical relations in the combination of acid and base by the wool also shows that the adsorption must occur on every molecule in the fiber.

2. *No recognition need be taken of differences in hydrogen-ion concentrations inside and outside the fiber.* This may signify either that these concentrations are identical, or that they are related to one another in a way which is practically independent of the presence of other ions. The assumption appears to be incompatible with the conventional application of the Donnan treatment to two-phase systems. Nevertheless, it represents a reasonable approximation, if postulate 1 given above is accepted: the existence of partially undissociated protein-chloride combinations would greatly minimize the differences predicted by the Donnan equations for the case of the combination of hydrogen ions alone. Since pH differences are the essential feature of the usual application of the Donnan equilibrium to fiber problems, disregard of this necessarily complicated and, in the present case, arbitrary treatment requires no further *a priori* justification.

Alternatively, postulate 1 may be regarded as a purely empirical way of evading explicit treatment of pH differences brought about by combination of the fiber protein with hydrogen ions alone. As will be shown later, both methods of calculation lead to very similar descriptions of a large part of the experimental phenomena, and a final choice between them can only be made on the basis of a wider field of observation, including comparisons with similar results with soluble proteins and with other insoluble materials, and the effects of other experimental variables which are still under investigation. In the meantime, the present treatment possesses a great advantage in simplicity of calculation.

[16] The assumption that the mass-action law may be applied implies that the fiber is a dispersed phase. In this case, the fiber must be thought of as a solid solution or as a solution of protein in imbibed water. If, on the other hand, the process of combination is one of adsorption, use of the Langmuir equation to describe it implies chemisorption at definite unsaturated points throughout the fiber; these points may be identified with the acidic and basic groups. Neither alternative involves new assumptions; the validity of one or the other is implied by the familiar experimental fact that the curves of acid combination by wool immersed in water are continuous and free of singular points. Derivations based either on the law of mass action or on the Langmuir adsorption equations necessarily lead to the same result.

The present treatment makes no assumption that the dispersed wool protein is a single chemical individual.

3. *Variation of activity coefficients in the fiber phase may be disregarded.* This is the only procedure possible when the system is not accessible to direct measurement by independent means. The postulate is required only if the law of mass action rather than the Langmuir adsorption equation is used.

It is implied in postulate 1 that an equilibrium,

$$WCl^+ \rightleftharpoons W^\pm + Cl^-, \tag{1}$$

in which $W^\pm$ represents wool in the uncombined state, occurs in addition to the more familiar acid-base equilibrium which may be written

$$WHCl \rightleftharpoons WCl^- + H^+. \tag{2}$$

If these are the only two equilibria which can occur and if, for simplicity, wool is regarded as a divalent ampholyte, that is, capable of combining a single equivalent of acid or a single equivalent of base, and two thermodynamic dissociation constants K_A' and K_B' are assigned to the equilibria 1 and 2 listed above, the law of mass action (plus postulate 3) or the Langmuir adsorption law permits us to write

$$\frac{[WHCl]}{[WHCl]+[WCl^-]+[W^\pm]} = \frac{1}{1+\frac{K_B'}{a_H}\left(1+\frac{K_A'}{a_{Cl}}\right)}. \tag{3}$$

The bracketed quantities represent concentrations, a_H and a_{Cl} the activities of hydrogen and chloride ions, respectively, and the left-hand member represents the fraction of the total wool combined with acid.

The resemblance of eq 3 to the familiar expression for the ionization of a dibasic acid is apparent. If account is also taken of the hydrogen ions removed from the external solution by absorption in the fiber in an amount equivalent to the negative charge contributed by combined chloride ions, the ratio of acid taken up to total wool becomes

$$\frac{[WHCl]+[WCl^-]}{[WHCl]+[WCl^-]+[W^\pm]} = \frac{1}{1+\frac{K_B'K_A'}{a_{Cl}(a_H+K_B')}}. \tag{3'}$$

Obviously the successive stages of combination might be formulated with equal *a priori* validity in the alternative equilibria:

$$WH^+ \rightleftharpoons W^\pm + H^+ \tag{4}$$

$$WHCl \rightleftharpoons WH^+ + Cl^- \tag{5}$$

to which the dissociation constants K_B and K_A may be successively assigned. The corresponding form of eq 3 is then

$$\frac{[WHCl]}{[WHCl]+[WH^+]+[W^\pm]} = \frac{1}{1+\frac{K_A}{a_{Cl}}\left(1+\frac{K_B}{a_H}\right)}, \tag{6}$$

and the corresponding form of eq 3′, which represents more closely the measured quantities, is

$$\frac{[WHCl]+[WH^+]}{[WHCl]+[WH^+]+[W^\pm]}=\frac{1}{1+\frac{K_B K_A}{a_B(a_{Cl}+K_A)}}. \qquad (6')$$

The four dissociation constants which appear in these equations are obviously interrelated as follows:

$$K_A K_B = K_A' K_B'.$$

Equations 3′ and 6′ differ from one another by the omission of different single terms in a complete expression for the sum of all the ionic states of the wool. This omission leads them to describe quite different relations between the hydrogen-ion and chloride-ion concentrations at which equal amounts of acid are taken up. Since there is no compelling reason for choosing between them, it is necessary to take both sets of equilibria into account in deriving the most general expression for the fraction of the maximum amount of acid bound as a function of a_H and a_{Cl}. This may be done in two ways, according to whether $[WH^+]$ is larger or smaller than $[WCl^-]$, since only the larger one of these two terms must be included in the numerator of the left-hand fraction, which expresses the part of the wool which binds acid. When $[WH^+]$ is the larger, the positive charge on the fiber is partly neutralized by the smaller term $[WCl^-]$ and partly by chloride ions in an adsorption layer.[17] Within the range of pH, and salt concentrations to which attention is here confined, and with any assignment of physically reasonable values to K_B' and K_A', $[WH^+]$ will be larger than $[WCl^-]$ and should therefore be chosen for inclusion in the numerator. This choice, implying $K_B \ll K_A'$, leads to the relation:

$$\frac{[WHCl]+[WH^+]}{[WHCl]+[WH^+]+[WCl^-]+[W^\pm]}=\frac{1}{1+\frac{K_B'}{a_B}\left(\frac{a_{Cl}+K_A'}{a_{Cl}+K_A}\right)}. \qquad (7)$$

The right-hand member of eq 7, like that of eq 3, which it closely resembles, differs from the expression for the dissociation residue of a monobasic acid only by the presence of the term in parentheses. In the presence of a constant concentration of chloride ions, this term is constant. Under these conditions the amount of undissociated acid varies with pH exactly as in the case of a monobasic acid, but the apparent strength of the acid (the position of the curve on the pH axis) varies with the magnitude of the bracketed term, which in turn depends on the concentration of chloride ions. With high anion concentrations the term in parentheses approaches a limiting value of unity, and the dependence of the acid bound at any given pH on further increases in the anion concentration disappears. Thus the limiting position of the titration curve is determined solely by K_B' and should correspond with the position of the titration curve of a

[17] With dye anions of high affinity for wool fibers, such as those used in substantive dyeing, it would be necessary to substitute in the numerator a term analogous to $[WCl^-]$ in place of $[WH^+]$. When more than one kind of cation is present, however, (in the presence of salt), this simple substitution does not suffice. The considerably modified relations which are applicable to cases in which $K_A' < K_B$ are beyond the scope of the present paper.

similar *dissolved* acid. It has already been shown that these properties of eq 7 correspond to experimental facts.[18]

The quantitative dependence of the positions of the titration curves described by eq 7 on the level at which the anion concentration is held constant may be demonstrated by determining the pH for half-maximal combination as a function of the anion concentration. This may be done by equating the right-hand member of eq 7 to 0.5. The resulting relation is

$$pH_{\frac{1}{2}} = pK_H' + \log\left(\frac{a_{Cl}+K_A}{a_{Cl}+K_A'}\right) \tag{8}$$

In addition to the relation $K_H \ll K_A'$ already discussed, electrostatic considerations obviously require that $K_A' > K_A$ (and $K_H > K_H'$). Thus, in the range $K_A' \gg a_{Cl} \gg K_A$, the logarithmic term approaches $\log \frac{a_{Cl}}{K_A'}$, and the pH for half-maximal combination, which characterizes the position of the entire acid-combination curve, shows a close approximation to direct dependence on the logarithm of the concentration of chloride ions. This range of direct dependence extends down to the lowest possible values of a_{Cl} (equal concentrations of hydrogen and chloride ions). The upper limit of this range is determined by K_A', which determines the concentration of anions at which a limiting position of the curve is approached.

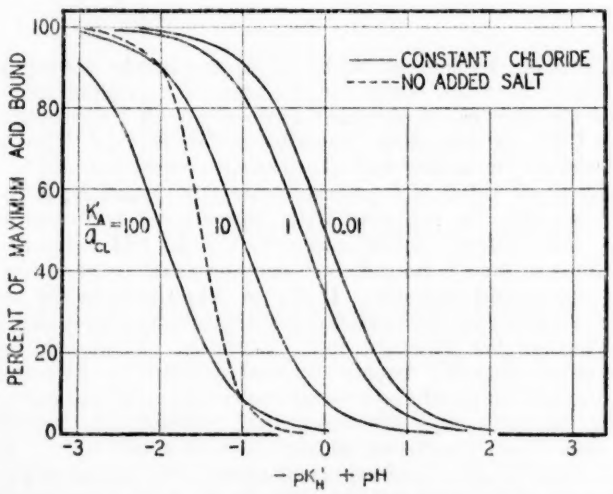

FIGURE 6.—*Theoretical curves of acid combination described by equations 7 and 7'.*

The effect of variations in ionic strength is demonstrated by representation of curves for four different values of K_A'/a_{Cl}.

The properties of eq 7 are illustrated in figure 6, which shows the theoretical curves of acid combination with respect to pH at several different values of K_A'/a_{Cl}. For purposes of calculation, K_A has been

[18] Thus, it is K_H' rather than K_H which corresponds to the dissociation constant of the acid in solution. This seems to imply that (in dilute solutions) K_H' is as little dependent on the nature of the anion as K_H. If this is true, the absolute values of K_A and K_A' can depend on the nature of the anion, but the ratio K_A/K_A' cannot. The conclusion is a reasonable one if the difference between K_A and K_A' or K_H and K_H' is attributed almost entirely to an electrostatic effect due to a single charge.

taken as vanishingly small, since $K_A' \gg K_A$. It is noteworthy that the assignment of an infinitely small value to K_A would make the right-hand members of eq 7 and 3 identical.

It is clear that the positions of the curves are determined by K_A'/a_{Cl}, although their shapes are independent of this ratio. The dependence of the positions on $\log K_A'/a_{Cl}$ is at first linear, but becomes less marked as the ratio diminishes; finally, at very low values of the fraction (a_{Cl} large), the positions of the curves approach a limit, determined by K_H'. By utilizing eq 8, K_A' may be roughly evaluated from the pH differences at the midpoints of curves at two or more different salt concentrations sufficiently high to be beyond the region of simple stoichiometric dependence.

In solutions containing no added salt, a_{Cl} is not constant but equal to a_H. Equation 7 then becomes

$$\frac{[WHCl]+[WH^+]}{[WHCl]+[WH^+]+[WCl^-]+[W^+]} = \frac{1}{1+\frac{K_H'}{a_H}\left(\frac{a_H+K_A'}{a_H+K_A}\right)}. \qquad (7')$$

Since K_A' has already been assumed to be large, and K_A very small, there is a wide range of values of a_H in which the bracketed expression reduces to K_A'/a_H. The curve in the absence of salt is then described, up to moderately high acidities and high degree of combination, by the relation

$$\text{Fraction of maximum acid bound} \doteq \frac{1}{1+\frac{K_H'K_A'}{a_H^2}}, \qquad (7'')$$

which is entirely consistent with the approximate description mentioned earlier: that the curve for the case of no added salt could be related to the curves at constant ionic strength by substitutions of $[H^+]^2$ for $[H^+]$ in functions describing the latter. The curve in figure 6 labelled "no added salt" is drawn to represent eq 7'. K_A' has been taken to be 1,000 K_H' (approximately 0.1) and K_A is considered negligibly small. In contrast with the curves for constant ionic strengths, the value of K_A' affects not only the pH value at which a given amount of acid is bound, but also the exact form of the relation between acid bound and pH. If K_A' is taken sufficiently small, the no-salt curve loses its characteristic steepness and becomes identical with the curves for constant ionic strength. Thus two additional means of estimating K_A' become available: (1) The difference in pH between the midpoint of the no-salt curve and any one curve at constant ionic strength, and (2) The extent to which the no-salt curves differ in slope from the curves at constant ionic strength. The value of K_A' selected for graphical representation in the no-added-salt curve of figure 6 (approximately 0.1) was chosen because it gives very nearly the proper separation from the other curves when the same value is substituted into the value of K_A'/a_{Cl} attached to each of them.

The most exacting of the remaining tests which could be applied to the consequences developed from the postulates would be to attempt superposition of the several sets of data with the theoretical curves described by eq 7 or 7'. These equations, however, were derived for the simplest case of monovalent acids; and wool, like other proteins, is highly polyvalent. This difference can have either

of two results: (1) If all the dissociating groups have identical *intrinsic* dissociation constants and if they are far enough removed from one another in the molecule to exclude appreciable electrical interaction between them, the acid-combining curves, as Simms [40], Weber [51], von Muralt [49], and others have shown, should be identical with those of a monobasic acid, and eq 7 and 7′ should be applicable. (2) If the groups are of unequal intrinsic strength, or if they are of equal intrinsic strength but are close enough to one another so that changes in distribution of electric charges, caused by partial dissociation, weaken the dissociating tendency of the remaining groups, the resulting acid-combination curve would be the sum of a number of smaller curves distributed along the pH axis. Consequently, it would be broader with respect to the pH axis than those predicted by the equations above.

In the direct comparison presented in figure 7, the estimated contribution of the imidazole groups (0.03 millimole) has been subtracted

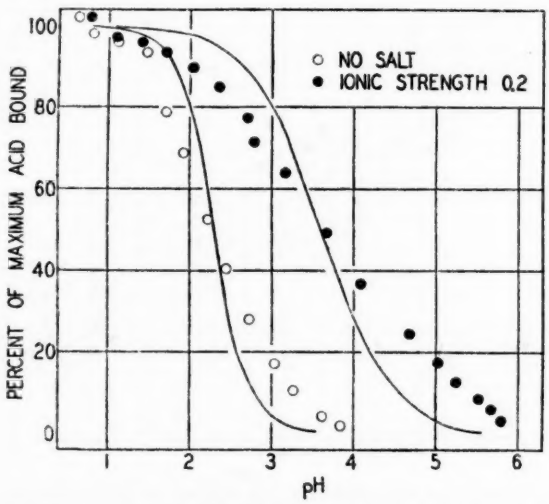

FIGURE 7.—*Experimental data for acid combination as a function of* pH *compared with theoretical curves for a mono-acid base (eq 7 and 7′).*

An estimated contribution from the histidine content of 0.03 millimole/g has been subtracted from the experimental values, as described in the text.

from the acid-combination data in an effort to have them represent as nearly as possible only the dissociation of carboxyl groups.[19] As the figure makes clear, the corrected experimental curves, both in the presence and absence of salt, are broader than the theoretical ones, and the second of the two alternatives stated above must prevail.

The high degree of symmetry of the differences between the experimental and the theoretical curves suggests, however, that the experi-

[19] The subtraction of a constant quantity is justified only at pH values more acid than those at which imidazole groups begin to give off hydrogen ions. In 0.2 *M* salt solutions, the correction should diminish appreciably at pH 5.4 and become zero at pH 6.4. Since the pH at which the correction would diminish in solutions low in salt or containing no salt cannot be estimated, recourse has been had to the subtraction of a quantity independent of pH. This results in varying degrees of overcorrection at the low end of each set of data, but the effect is small.

mental curve is not the sum of a small number of distinct groups of curves characterized by *widely different* dissociation constants, but is the result of a very regular kind of electrostatic interaction between ionic charges affecting the dissociation of groups which are all intrinsically similar. Earlier analyses of the acid-titration curves of other proteins [5, 8, 9, 10, 17] have been based on the opposite assumption of distinct groups characterized by widely different constants.

The view suggested above is based on considerations similar to those which led Cannan to the same conclusion for the titration curve of egg albumin; it receives added support from the fact that the midpoint of the experimental curve (at high salt concentrations) occurs at a pH (4.0 to 4.1) which may be expected to characterize the dis-

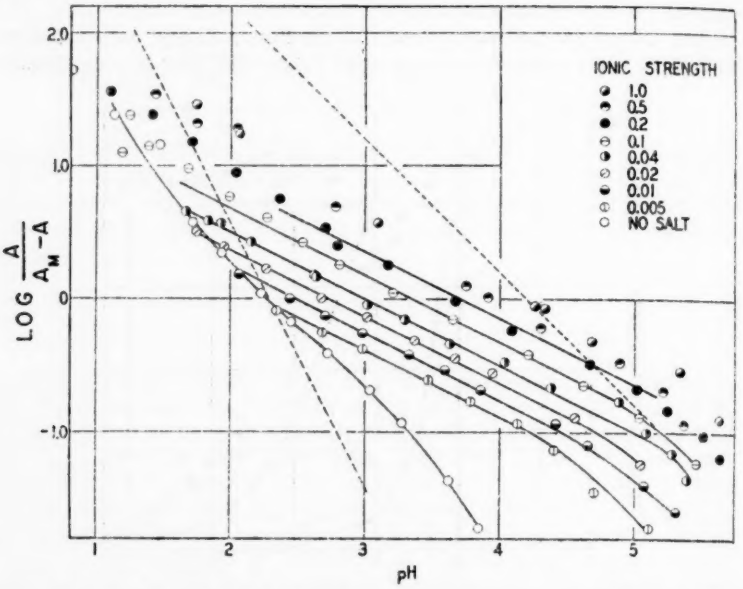

FIGURE 8.—*Experimental data for acid combination as a function of* pH *and chloride concentration (corrected by subtraction of the estimated contribution of histidine) compared with the linear relations described by equations 7 and 7′.*

The straight lines through the experimental points over the range of approximately 5 percent to 90 percent of maximal combination were drawn with a slope of 0.5. The broken lines represent the theoretical equations for no-salt (7′) and for infinite salt [7], respectively.

sociation of carboxyl groups in large peptides [6], and by other considerations discussed below.

The regularity of the difference between the theoretical curve for a monovalent acid and the experimental curve is shown more clearly if the ordinates of all the curves, after subtraction of the estimated contribution of histidine, are changed from the acid bound to log $A/(A_m-A)$, where A signifies the amount of acid bound at any pH and A_m is the maximum acid-binding capacity. The resulting graphs of the measurements at constant ionic strength, shown in figure 8, are close approximations to straight lines which are roughly parallel over a wide part of their total range. Deviations from this regularity appear only where the maximum and zero values are approached,

but at both these extremes the quantity plotted is extremely sensitive to experimental error. In addition, the data may well deviate from this simple theoretical relation for acid combination as zero acid combination is approached, since the base combination function which begins to be of importance in this region has been left out of account. As a result of this additional factor, the curves must intersect at the base line within a narrow interval of pH, and cannot remain parallel.

The slope of the theoretical curve in figure 8 for constant ionic strength is -1.0. The slopes of the lines through the experimental points for ionic strengths up to 0.2 are exactly -0.50. Thus a very simple relation exists between the experimental data and the theo-

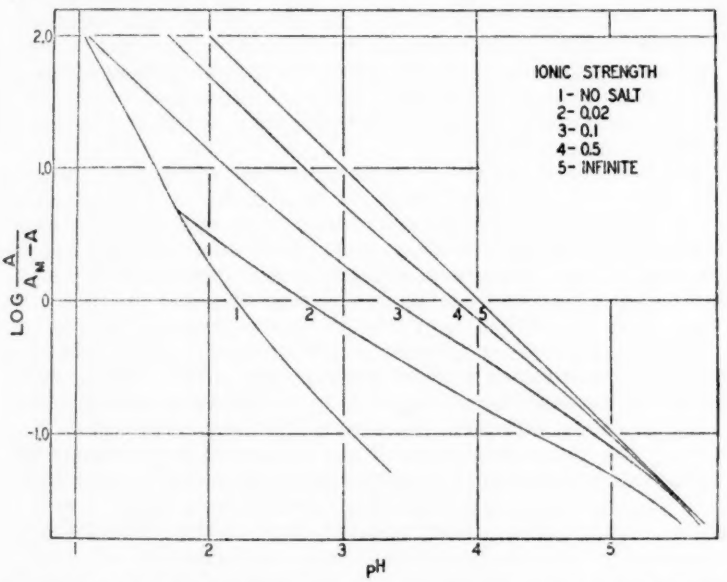

FIGURE 9.—*Effect of different constant anion concentrations on the acid bound by a nondiffusible base as a function of* pH.

The parameters employed in the application of the Donnan equations are given in the text.

retical curves, which were derived on the assumption of a single dissociation constant for all the dissociating groups. The simplicity of this relation appears to support the view that the curve is the sum of a *continuous* series of curves for the individual dissociating groups, which differ in strength from one another by slight increments determined by some law of electrical interaction between their charges, rather than that the curve is the sum of a few groups of identical curves with widely different constants.

The slope of the theoretical curve for no added salt (eq 7′) depends on the ratio of K_B' to K_A'. When $K_A' \gg K_B'$ (the more probable case with HCl), the slope approaches -2. When K_A' is only 10 times larger than K_B' the slope is still nearly -2 for small amounts of acid bound, but its absolute value becomes considerably smaller for larger amounts. However, the data obtained in the absence of salt, shown in figure 8,

have a slope of very nearly −1 when the amounts of acid bound are less than three-quarters of the maximum. For larger amounts bound, the slope approaches −2. It is not surprising that the discrepancy between the simple theory and the measurements should be more serious and less regular in the absence of salt than at constant ionic strength, since the dependence of acid bound on hydrogen ion concentration in eq 7′ or 7″ is essentially of higher degree than in eq 7. The transition (involving a summation) from the simple equation for a monovalent acid to the proper polyvalent equation is, therefore, more complicated.

The fact that over a great part of the pH range the slope obtained in the absence of salt is also just one-half of the value required by the equations has the fortuitous result that the experimental curve somewhat resembles the curve of the simple law of mass action for a monobasic acid [44]. This approximate resemblance must be regarded as the resultant of the opposing effects of the steepening of the curve caused by simultaneous variation of hydrogen and chloride ions, and the broadening effect of electrostatic interaction between many identical dissociating groups.

The hypothesis that the departure of the individual experimental curves from the slopes predicted by eq 7 and 7′ is caused solely by the high polyvalency of the wool protein, does not depend exclusively on the considerations just discussed. It is very strongly supported by the almost exact correspondence of the experimental curves for wool at high constant ionic strengths with the corresponding curves for egg albumin. When similarly plotted as log $A/(A_m-A)$ against pH these data (at least for dilute salt solutions) also yield straight lines, with slopes which are also very nearly −0.5. The same linear relationship between log $A/(A_m-A)$ and pH has appeared in investigations of widely different dissolved substances which have in common only the properties of polybasicity and high molecular-weight. These substances include, among others, polyacrylic acid [32], and certain nucleic acids [23, 41]. Kern has shown that, over a wide range of polymerization numbers, the slope of the linear relationship for polyacrylic acid is also almost exactly −0.50.

2. ALTERNATIVE ANALYSIS BY THE DONNAN EQUILIBRIUM

The difficulties inherent in application of the Donnan equations to the combination of wool fibers with acid have already been detailed. However, if a somewhat arbitrary selection of parameters is permitted, an alternative treatment for the restrictions on combination of acid due to the presence of two phases is possible, and a number of features of the present data can be described as direct consequences of the Donnan equations. In application of the Donnan equilibrium to fibers, a choice must be made between regarding the solid phase as a dispersed phase (in imbibed solvent), permeable to dissolved acid and salts, and the alternative view that it is a true solid phase in which the phenomena of acid combination take place in an external adsorption layer. The first of these models has been chosen as a basis for calculation, since the second offers no obvious basis for the assignment of any but arbitrary numerical parameters.

The result of this choice is given in figure 9, which shows calculated curves of acid combined by protein as log $A/(A_m-A)$. In this cal

culation a single dissociation constant, 1×10^{-4}, and a protein concentration of 0.8 equivalent per liter have been used. The latter value bears a reasonable relation to the equivalent weight of wool, which is approximately 1,250, and its moisture content at saturation which is approximately 30 percent by weight. Although the relations of the curves calculated for no added salt and for different constant ionic strengths would be appreciably altered by the choice of other numerical values, their positions on the pH axis and the value of the maximum fix the relation of the dissociation constant to the equivalent concentration within fairly narrow limits. Activity coefficients have been neglected. The ordinates of the curves represent only the acid reacting with the protein and do not include the acid which may be merely dissolved in the fiber phase. The latter should be practically negligible except in the immediate vicinity of the top of the curve.

It is immediately evident that the curves in figure 9 satisfy the requirements imposed by the data in three outstanding respects: (1) The curve for the case of no added salt is very similar to the experimental one. (2) The curves for constant ionic strengths are less steep than the curve for no salt, and their average slopes, although still too high, are nearer the experimental ones than the slopes given by eq 7, which were twice as large as those required by the data. (3) When measured in the upper half of the figure, the dependence on ionic strength of the pH values at which a given amount of acid is combined is approximately logarithmic when the ionic strengths are low; when the ionic strengths are high, the positions of the curves with respect to the pH axis approach a limit.

In another important respect, however, the curves of figure 9 are entirely different from those obtained by experiment or calculated from eq 7 (shown in fig. 8); the experimental curves are roughly parallel except at very high ionic strengths, and as they approach closely to the base line. The curves of figure 9, on the contrary, converge continuously, and this convergence is inherent in any simple analysis by means of the Donnan equilibrium.

Another consideration must be taken into account, before accepting as significant the partial agreement of the Donnan equations with experiment. It has already been shown that there is a detailed agreement between the experimental data for wool and for dissolved egg albumin at moderate ionic strengths. If significance were to be attached to the fact that the Donnan equations reduce the slope of the theoretical monobasic acid curve to a value considerably closer to its experimental value for wool, then it would seem necessary to conclude that the Donnan treatment must be applied also to egg albumin *in solution*. The further requirement that the application of the Donnan equations to the *dissolved molecules* must involve nearly identical numerical values for the parameters of the equations in the two physically quite distinct cases is even less acceptable.

The model which has been used as a basis for the application of the Donnan equations to the present experiments is intrinsically unreal. It is unlikely, for example, that all the water contained in the immersed fibers can be regarded as solvent water. Not only is it comparable in magnitude with the water of crystallization of proteins in general, but it corresponds closely with the hypothesis of definite and limited hydration of the polar groups or bonds of the wool molecule.[20]

[20] Unlike such cases as swollen gelatin to which the Donnan equations are more legitimately applied.

Such bound water can be regarded as a solvent medium only in a very restricted sense, and it is hardly likely that acids or salts will distribute themselves between it and the external solvent medium in a simple one-to-one ratio. It has not proved possible to detect experimentally any combination with neutral salts when fibers containing half of the maximum amount of water which they can absorb are placed in 0.2 *M* KCl at pH 6.4. Thus half or nearly half of the maximum water content is not free to dissolve ionized acids or salts. This conclusion also results from a recent detailed study of moisture absorption of cotton fibers in this laboratory [42].

The principal distinction for practical purposes (such as the interpretation of acid dyeing) between the mechanism of acid combination proposed in this paper and the alternative treatment in terms of the Donnan equilibrium, lies in the expectation that the specific affinities ($1/K_A'$) of different anions for wool may vary considerably. Conversely, the experimental study of such a variation and its dependence on such variables as temperature and dielectric constant has considerable bearing on the views discussed here, and is at present in progress.

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